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Treatment Effectiveness: Oil Tanker Ballast Water Facility

Rockwell International
Newbury Park, CA

Prepared for

Municipal Environmental Research Lab.
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TREATMENT EFFECTIVENESS: OIL TANKER BALLAST WATER FACILITY

by

Ihor Lysyj
Rockwell International Corporation
Newbury Park, California 91320

Contract Number 68-03-2648

Project Officer

John S. Farlow
Oil and Hazardous Materials Spills Branch
Municipal Environmental Research Laboratory - Cincinnati
Edison, New Jersey 08837

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16. ABSTRACT

A study dealing with the effectiveness of large-scale treatment of ballast water was conducted at the terminal facility of the TransAlaska Pipeline in Valdez, Alaska. The plant was found to be generally effective in reducing the petroleum content of the ballast water. On the average, the oil content of incoming ballast water (ranging between 7,000 and 10,000 ppm) is reduced to an organic load equal to 10 to 11 milligrams carbon per liter (mgC/L) in the final effluent. The bulk of the organic content reduction takes place in the gravity separators. Typically, the final treated effluent contains 45% to 50% volatile aromatic hydrocarbons, 35% to 40% dissolved nonvolatile organics, and 10% to 20% suspended organic matter.

It was found that the treated effluent did not mix uniformly with the receiving waters of Port Valdez during periods of thermal and density stratification. The maximum concentration of aromatic hydrocarbons was found at a depth of 50 meters in early summer and at a depth of 65 meters in late summer. The horizontal spread of hydrocarbon contamination extended as far as 2 to 3 kilometers (km) from the plant outfall.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report presents the results of the sampling and analysis of the influent and effluent from the unit processes of a large, modern treatment plant for processing oil tanker cargo ballast water. Also presented are the findings from less extensive field surveys designed to indicate the extent of the treated effluent plume in the receiving waters of the fjord. These results will be of interest to all those interested in the treatment of oil-contaminated water.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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ABSTRACT

A study dealing with the effectiveness of large-scale treatment of ballast water was conducted at the terminal facility of the TransAlaska Pipeline in Valdez, Alaska. The treatment plant performance evaluation was conducted during three separate 10-day periods: Summer 1978, Winter 1979, and again in Summer 1979.

The treatment plant was found to be generally effective in reducing the petroleum content of the ballast water. On the average, the oil content of incoming ballast water (ranging between 7,000 and 10,000 ppm) is reduced to an organic load equal to 10 to 11 milligrams carbon per liter (mgC/L) in the final effluent. The bulk of the organic content reduction takes place in the gravity separators. Approximately 99.8% of the petroleum present in the incoming ballast is removed there. The secondary treatment (dissolved aeration-flotation process) reduces the remaining organics by 30% to 50%.

The treatment produces changes in the chemical composition of the process stream. Unlike the neat crude oil, which is composed largely of aliphatic compounds, the organic composition in the treated ballast effluent is largely aromatic. Typically, the final treated effluent contains 45% to 50% volatile aromatic hydrocarbons (including benzene, toluene, xylenes, and ethylbenzene), 35% to 40% dissolved nonvolatile organics (including phenols and naphthalenes), and 10% to 20% suspended organic matter, which can be properly defined as "the oil," being composed of aliphatic hydrocarbons and other water-insoluble fractions of petroleum.

Because aromatic hydrocarbons were found in the treated effluent and significant amounts were discharged into the Valdez fjord, a limited fjord dispersion study was carried out. The treated effluent did not mix uniformly with the receiving waters of Port Valdez during periods of thermal and density stratification, at which times the volume of the mixing zone is under-utilized and no significant amount of hydrocarbons diffuse into the upper reaches of the water column. The maximum concentration of aromatic hydrocarbons was found at a depth of 50 meters in early summer and at a depth of 65 meters in late summer. The horizontal spread of hydrocarbon contamination extended as far as 2 to 3 kilometers (km) from the plant outfall.

This report was submitted in partial fulfillment of Contract No. 68-03-2648 by Rockwell International under the sponsorship of the U.S. Environmental Protection Agency. The study was conducted from April 1978 through November 1980, and work was completed as of January 1981.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii
Acknowledgments x

1. Introduction 1
2. Conclusions 4
3. Recommendations 6
4. Ballast Water Treatment Plant Study 7
    Introduction 7
    Methods 9
    Terminal Ballast Treatment Facility in Port Valdez, Alaska . 12
    Field Studies 15
    Results and Discussion 30
5. Fjord Study 48
    Introduction 48
    Port Valdez 49
    Experimental 55

References 67

Appendices

A. Analytical Scheme for Organic Material Balance in Oily Wastewaters. 68
B. Quality of the Data 76
C. History of Plant Operation 103
D. Experimental Data 107
E. Chemical Composition of Dissolved, Nonvolatile Fractions in Ballast Water 145
F. Comparative Evaluation of Standard and Modified Methods for Total Oil Determination 154
G. Aromatics in Oily Wastewaters: Determination of Benzene, Toluene, and Xylenes 161
H. Procedures used in Harbor Studies 167

BEGIN FIRST LINE OF TEXT HERE
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TOP OF IMAGE AREA
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FIGURES

Number		Page
1	Location of Port Valdez	9
2	Ballast water treatment plant block diagram	13
3	Volumes of aromatic hydrocarbons as a function of plant discharge rate	40
4	Location of outfall diffuser and mixing zone	50
5	Temperature, salinity, and density stratification in Port Valdez, summer conditions	52
6	Temperature, salinity, and density stratification in Port Valdez, winter conditions	53
7	Diffuser tests (approximate areal extent of observed minimum dilutions less than 80).	57
8	Concentration decay of aromatic hydrocarbons in vertical plane, Station 42, Port Valdez, Alaska, September 1979.	59
9	Harbor sampling stations, September 12-13, 1979	61
10	Decay of aromatic hydrocarbons in vertical plane, Station 42, Port Valdez, Alaska	64

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PAGE NUMBER
EPA Form 2300-4 (4-80)
(PREVIOUSLY EIR: EPA FORM 337)
TYPING GUIDE SHEET

TABLES

Number		Page
1	Chemical Composition of Effluent from Gravity Separator, Summary, August 17-18, 1978	16
2	Chemical Composition of Final Effluent, Summary, August 7-16, 1978	17
3	Range of Concentrations in the Final Effluent, August 7-16, 1978	18
4	Reduction of Organic Content in Process Water by the Secondary Treatment Process, Port Valdez, Alaska, August 7-18, 1978	19
5	Chemical Composition of Untreated Ballast, Summary, February 19 - March 2, 1979	21
6	Chemical Composition in Effluent from Gravity Separator, Summary, February 19 - March 2, 1979	22
7	Range of Concentrations in the Primary Effluent, February 19 - March 2, 1979	22
8	Chemical Composition of Final Effluent, Summary, February 19 - March 2, 1979	23
9	Range of Concentrations in Final Effluent, Summary, February 19 - March 2, 1979	23
10	Stepwise Reduction of Organic Content in Process Water by the Treatment Process, February 19 - March 2, 1979	25
11	Chemical Composition of the Effluent from the Gravity Separator, Summary, June 19-30, 1979	27
12	Range of Concentrations in the Gravity Separator Effluent, June 19-30, 1979	27
13	Chemical Composition of the Final Effluent, Summary, June 19-30, 1979	28
14	Range of Concentrations in the Final Effluent, Summary, June 19-30, 1979	28

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 257)
TYPING GUIDE SHEET

TABLES (Continued)

Number Page

15 Reduction of Organic Content in Process Water by the Treatment Process, Port Valdez, Alaska, June 19-30, 1979 29

16 Compositions of Primary and Final Effluents, Valdez, Alaska Ballast Water Treatment Plant, Summary, August 1978 - June 1979 31

17 Stepwise Reduction of Organic Content in Process Water by the Treatment Process, Port Valdez, Alaska, Summary, August 1978 - June 1979 33

18 Average Chemical Compositional Changes in the Process Stream. . 34

19 Estimated Daily Discharge of Organic Matter, First Summer Study, August 1978 36

20 Estimated Daily Discharge of Organic Matter, Winter Study, February 1979 37

21 Estimated Daily Discharge of Organic Matter, Second Summer Study, June 1979 38

22 Average Daily Discharge (in Liters) of Volatile Hydrocarbons During Summer 1978, Winter 1979, and Summer 1979 Studies . . 39

23 Discharge Volumes During First 2 Years of Treatment Plant Operations 41

24 Monthly Volumes of Ballast Processed and Average Concentrations of Oil and Grease (by Gravimetric Method) 43

25 Average Daily Discharge of Organic Matter from the Terminal Treatment Facility 44

26 Relationship Between Total Organic Load and Extraction-IR and Extraction-Gravimetric Methods for Total Oil 45

27 Relationship Between Total Organic Load and Total Oil Determination 46

28 Monthly Record of Discharges of Treated Ballast Water, First and Second Years of Plant Operation, Terminal Facility, Valdez, Alaska 54

29 Aromatic Hydrocarbons in Valdez Harbor, July 1-6, 1979 58

30 Aromatic Hydrocarbons in Valdez Harbor: Vertical Distribution . 58

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EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 237)
TYPING GUIDE SHEET

TABLES (Continued)

Number		Page
31	Aromatic Hydrocarbons in Valdez Harbor: Near-Bottom Environment	60
32	Aromatic Hydrocarbons in Valdez Harbor: Horizontal Distribution Outside the Diffuser Zone at 60-Meter Depths .	62
33	Aromatic Hydrocarbons in Port Valdez: Vertical Distribution, June 1980 Study	63
34	Aromatic Hydrocarbons in Port Valez: Horizontal Concentration Decay, June 1980 Study	65
35	Aromatic Hydrocarbon Profile in Port Valdez, June 1980 Study .	66

EPA Form 2350-4 (4-80)
(PREVIOUSLY C.I.N. EPA FORM 257)
TYPING GUIDE SHEET

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The fjord study was carried out with the cooperation and assistance of the National Marine Fisheries Service, NOAA, which provided a vessel, operating personnel, and sampling equipment; and the U.S. Coast Guard, which provided access to the security zone of the Alyeska terminal facility.

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The research teams conducting this study were:

Summer 1978 Study - Ihor Lysyj, Ronald Rushworth, Robert Melvold (Rockwell International) and Joseph LeBeaux (Department of Environmental Conservation, State of Alaska).

Winter 1979 Study - Ihor Lysyj, Matthew Yoong, and George Perkins (Rockwell International).

Summer 1979 Studies - Ihor Lysyj, George Perkins, Kathy Doering, and David Janka (Rockwell International).

EPA Form 2350-4 (4-80)
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SECTION 1

INTRODUCTION

The principal objective of this study was to determine how effective the present state-of-the-art technology is in complying with existing government regulations regarding the discharge of treated oily wastewater. In addition, an attempt was made to generate new information and data on the chemical composition of oily wastewater, compositional changes in the process stream, and the quality of the final treated effluent in terms of total organic content (including free oil, dissolved nonvolatile organic material, and volatile hydrocarbons).

A large-scale ballast treatment plant in Valdez, Alaska, was selected for this study. The plant, which is operated by the Alyeska Pipeline Service Company, became operational in August 1977, and its discharge is regulated by the NPDES permit issued by the U.S. Environmental Protection Agency (EPA) and the Department of Environmental Conservation, State of Alaska. The oil-water separation process includes primary treatment by gravity separation, followed by dissolved air flotation, pH adjustment, and retention in polishing ponds.

The treatment plant performance evaluation was conducted during three separate periods: Summer 1978, Winter 1979, and again in Summer 1979. A chemical laboratory was set up in the office of the Department of Environmental Conservation, State of Alaska, and most tests were performed there. In addition to conventional analysis for oil and grease by standard methods, an analytical protocol for gross and detailed chemical characterization of process water was developed and used in this study. The protocol was based on total organic content determination and involved determination of suspended organic matter, volatile hydrocarbons, and dissolved nonvolatile organic matter. The sum of those three fractions constitute total organic load of the process stream. In addition, the volatile hydrocarbon fraction was characterized by GC and GC-MS analyses, and composition of the dissolved nonvolatile fraction was profiled by HPLC analysis. Using this protocol, it was possible to establish the material balance for all three physical states of organic matter present in the process stream.

The results of this study indicate that the treatment plant was effective in reducing the free oil content of the ballast water. A reduction of over 99.8% in the organic load was realized, producing effluent generally within federal regulations regarding discharge of the oil. Seasonal variations appear to have little effect on the treatment process, and the water quality of the final effluent observed during the summer and winter months of operation was remarkably similar. The bulk of organic content reduction took place in the gravity separator, whereas the dissolved aeration flotation unit added relatively little to the treatment process.

Also, the treated effluent was found to contain a substantial amount of petroleum-derived organic matter, which is not controlled by current federal regulations. Specifically, it was found that an average chemical composition of treated effluent was as follows:

	mgC/L	%
Benzene	2.0	19
Toluene	1.8	17
Xylenes/Ethylbenzene	0.9	8
Aliphatic Hydrocarbons	0.2	2
Total Volatile Hydrocarbons	4.9	46
Total Dissolved Organics	4.3	40
Total Suspended Organics	1.5	14
Average Total Organic Load of the Effluent	10.7	100

Because of the large volumes of ballast processed, significant amounts of aromatic hydrocarbons are discharged by the plant on a daily basis. Based on plant discharge records and experimental data generated by this study, it can be estimated that the average daily discharge of aromatic hydrocarbons by the plant is between 230 and 260 liters, and that during the 2 years of plant operation, approximately 175,000 liters of aromatic hydrocarbons were discharged into Valdez fjord. The dissolved nonvolatile organic matter was not removed by the treatment process, and a significant amount of naphthalenes and phenols were also discharged.

In addition, a limited study was carried out in Valdez fjord. This study addressed the dispersion and dissipation of aromatic hydrocarbons in receiving waters. Vertical and horizontal transect samples were collected in the mixing zone near the plant outfall and at seven sampling sites in the harbor.

The treated effluent does not mix uniformly with the receiving waters of Port Valdez during periods of thermal and density stratification, at which times the volume of the mixing zone is under-utilized and no significant amount of hydrocarbons diffuse into the upper reaches of the water column. The maximum concentrations of aromatic hydrocarbons were found in late summer, within 10 meters of the bottom in the area of the mixing zone, stretching in the horizontal plane at a 60-meter depth as far as 2 to 3 km from the plant outfall. The maximum concentration level of hydrocarbons in early summer was at a 50-meter depth. Concentrations of aromatic hydrocarbons as high as 120 micrograms/liter (ppb) were found at the mixing zone boundary in the near-bottom environment. The levels of pollutants, however, declined rapidly in the vertical plane.

It is concluded that while current state-of-the-art oily wastewater treatment technology (as practiced by the Alyeska Pipeline Service Company in Valdez, Alaska) is capable of meeting federal regulations regarding discharge of oil and grease, it is inefficient in removal of other petroleum-derived organic materials, including volatile aromatic hydrocarbons and dissolved nonvolatile organic matter.

SECTION 2

CONCLUSIONS

As a result of the three-part study dealing with the operation of the large-scale on-shore ballast treatment facility in Port Valdez, Alaska, the following conclusions can be drawn.

1. The treatment plant is effective in reducing petroleum content of ballast water. On the average, an estimated 7,000 to 10,000 milligrams per liter (mg/L) of oil in incoming ballast is reduced to an organic load corresponding to 10 to 11 milligrams carbon per liter (mgC/L) in the final effluent. This value reflects total organic material load in the effluent and should not be confused with the oil and grease content of the sample.

2. The bulk of organic content reduction takes place in the gravity separator. Approximately 99.8% of the petroleum present in the incoming ballast is removed by this process unit. Suspended organic matter consisting of aliphatic hydrocarbons and other water-insoluble fractions of petroleum are removed here.

3. Secondary treatment based on dissolved aeration-flotation was found to be a minor contributor to the removal of the oil. This unit process is designed primarily for removal of water-insoluble petroleum (free oil). The bulk of free oil, however, is removed quite efficiently by the gravity separator, before aeration-flotation treatment.

4. Seasonal variations appear to have little effect on the treatment process. The water quality of the final effluent observed during the summer and winter months of operation was remarkably similar.

5. The treatment changes the chemical composition of the process stream. The organic composition of the treated effluent is largely aromatic.

6. Volatile aromatic hydrocarbons constitute almost half of all organic compounds present in the treated effluent. The principal compounds present are benzene, toluene, xylenes, and ethylbenzene. The non-volatile dissolved fraction (35% to 40% of the total organic load) contains significant amounts of phenols, naphthalene and its derivatives. Higher aliphatic hydrocarbons and other petroleum water-insoluble compounds contribute only 10% to 20% of the total organic load of the treated effluent.

7. Because of the large volume of ballast processed, significant amounts

of aromatic hydrocarbons and nonvolatile organic compounds are discharged daily. The daily average discharge of aromatic hydrocarbons during 2 years of treatment plant operation was estimated to be 230 to 260 liters. All in all, approximately 175,000 liters of aromatic hydrocarbons were discharged between August 1977 and August 1979 into the receiving waters of Port Valdez.

8. Because treated effluent and the process stream contained large proportions of volatile hydrocarbons, standard analytical methods for oil and grease appear to be not very effective in process monitoring or in determining water quality of the final effluent. This is because the volatile fraction of the oil is lost in the gravimetric procedure, while the IR method is less sensitive to aromatic hydrocarbons that comprise the bulk of hydrocarbons in the process stream.

9. Fjord studies carried out in June/July and September 1979 and in June 1980 indicate that the treated effluent discharged from the terminal facility (as measured by its aromatic hydrocarbon content) does not mix uniformly with the receiving waters of Port Valdez during periods of thermal and density stratification. During these times the volume of the mixing zone is grossly under-utilized, and no significant amount of hydrocarbons penetrate into the mixing zone in the vertical direction. The maximum concentration of aromatic hydrocarbons was found in late summer months within 10 meters of the bottom in the area of the mixing zone, stretching in the horizontal plane as far as 2 to 3 km from the plant outfall.

10. The results of the fjord study generally conform to predictions by Hood (1) and observations by Colonell (2), who reported the existence of a "trap depth" of 50 to 60 meters in the receiving waters of Valdez Harbor during the summer months.

11. An explanation for the observed phenomenon could possibly be found in studies by Quay and Broecker (3), who reported that "for a given lake, the rate of vertical mixing is inversely related to density gradient." Examination of density isobars for summer months in Port Valdez indicate that extensive density stratification reaches an approximate depth of 60 meters. This highly stratified water column above the treatment plant outfall might prevent vertical diffusion of the effluent, resulting in a "pancake-type" spread of pollutants just below the thermocline across the water body of the harbor.

12. The studies reported here were carried out only during the summer months. Different patterns of diffusion probably exist during late fall and late spring when water turnovers in the harbor occur, and during the long winter period when waters of the harbor are uniformly mixed and do not exhibit any degree of thermal or density stratification. The exact nature of the diffusion pattern in Port Valdez during periods other than summer months is unknown at this time.

SECTION 3

RECOMMENDATIONS

1. Substitute options for secondary treatment that are more effective in removal of volatile and water-soluble organics should be considered in future designs of ballast treatment facilities.

2. Future research in this field should address methods for reducing aromatic (volatile and nonvolatile) content of the process stream.

3. Monitoring of the quality of the final effluent should be based on total organic material balance and should include determinations of volatile, dissolved, and suspended organic fractions.

4. The impact of aromatic hydrocarbon discharge on the biota of the receiving waters should be determined.

5. The path and method of aromatic hydrocarbon dissipation in Port Valdez should be systematically studied as a function of prevailing hydrological conditions. This will require measurement of concentration decay of aromatic hydrocarbons in the vertical and horizontal planes during a 1-year climatic cycle. Field studies should be carried out at 1- to 2-month intervals.

6. The generated data should be related to the input of aromatic hydrocarbons into the receiving environment of Port Valdez from the Alyeska ballast treatment plant, and the relationship between system input and output (assimilation) should be established.

7. The extent and fluctuation (in dimensions) of the contaminated zone should be delineated and used for the prediction of possible effects on biota in the receiving zone.

8. Diffusion patterns should be studied in the proposed outfall area of the proposed Alpetco refinery.

SECTION 4

BALLAST WATER TREATMENT PLANT STUDY

INTRODUCTION

With the passage of the Federal Water Quality Improvement Act of 1970 (33USCA, 1161 et seq., April 3, 1970), Congress declared that it is the policy of the United States that there should be no discharges of oil into or upon the navigable waters of the United States, adjoining shorelines, or into or upon the waters of the contiguous zone. This policy was strengthened by the Federal Water Pollution Control Act Amendments of 1972. It also called for the President to issue regulations defining that quantity of oil which will be harmful. The regulations were published by the Secretary of the Interior on September 11, 1970 (35 "Federal Register," 14307). These regulations prohibit discharges of oil in quantities harmful to the public health and welfare and which (a) violate applicable water quality standards, or (b) cause a film or sheen upon or discoloration of the surface of water or adjoining shorelines, or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines. Nineteen states currently have stringent laws dealing specifically with oil pollution, and all states have general water quality regulations dealing with oil discharges. A number of foreign countries (including NATO countries, Japan, etc.) also have or are formulating strict oil pollution control laws.

More recently (February 1979), the State of Alaska issued specific regulations (4) regarding the discharge of petroleum hydrocarbons, oil and greases. According to those regulations, in the areas designated for growth and propagation of fish, shellfish, other aquatic life, and wildlife, including waterfowl and furbearers, total hydrocarbons in the water column shall not exceed 15 micrograms per liter and total aromatic hydrocarbons shall not exceed 10 micrograms per liter.

As a result of these and other government regulations, a widely used practice of overboard discharge of untreated bilge or ballast waters came to an end. To cope with the new requirements, both on-board and on-shore oil-water separation practices became common. Coalescence devices are widely used today for on-board oil-water separation, while gravity separation, sometimes assisted by aeration-flotation operations, are used to a great extent in on-shore ballast and bilgewater treatment operations.

The simplest form of oily waste treatment involves gravity separation of oil from water in holding tanks, ponds, or other suitable vessels. The separation step is usually followed by skimming of the surface oil film and discharge of the separated water to the environment. More complex operations assist gravity separation by the air or gas flotation. The flotation step is often augmented by the addition of flocculating agents and may be followed by additional gravity separation as a safety precaution. The presently used methods are physical treatment and are based on the specific gravity differential between water and oil.

The size of on-shore treatment facilities ranges from relatively small, treating less than 1000 gallons of bilgewater per day (5), to large-scale operations handling millions of gallons of ballast water a day, such as is the case in this study.

The largest of all on-shore ballast treatment installations was put into operation in August 1977 in Port Valdez, Alaska, which is located in the northernmost part of Prince William Sound in Alaska (Figure 1). This was necessary because of initiation of full-scale operation of the Trans-Alaska Pipeline, and a requirement for the safe and ecologically sound discharge of large volumes of ballast into the receiving waters of Port Valdez. Oil Tankers arrive from southern ports partially loaded with ballast water (up to 40% of the tanker's capacity) (6). The ballast water is discharged in Port Valdez and the tankers are reloaded with Prudhoe Bay crude for shipment south. During the first year of plant operations, an average daily water discharge rate was approximately 40 million liters. In August 1978 during the days of the first summer study, the average rate of discharge was 49 million liters a day, while during the Winter 1979 study, the average discharge rate rose to 91 million liters per day. During the second summer study in June 1979, the average daily discharge rate was 49 million liters.

The facility for treatment of this wastewater has been designed and built using the latest technology available for treating oily wastes. The method of treatment is based on a scale-up of oily water treatment processes that have been used for a number of years for processing produced water from on-shore and off-shore oil extraction operations. The principal units in this scheme are gravity separators and secondary units of chemically aided, dissolved air flotation. The effluent holding reservoir can be considered as a third unit of operation.

The object of this study was to determine the capabilities and limitations of a modern, state-of-the-art oily waste treatment plant in dealing with ever-increasing quantities of waste from energy-related operations.

In order to conduct this study, it was necessary to establish a chemical laboratory in Valdez, Alaska, to run the majority of tests and analyses on-site. Such a laboratory was established with the assistance of the State of Alaska, Department of Environmental Conservation, in the Court Building, Valdez, Alaska. In addition to the usual laboratory equipment, the following instrumentation was installed and put into field operation: Beckman TOC analyzer, Perkin-Elmer infrared spectrometer, Gow-Mac gas chromatograph with hydrogen flame ionization detector, ultrasonic probe, Millipore filtration assembly, gas sparging apparatus, liquid chromatographic assembly, and liquid-liquid extraction apparatus. The equipment was delivered to Valdez in June, installed and put into operation in July, and a full-scale test program was undertaken during the month of August 1978.

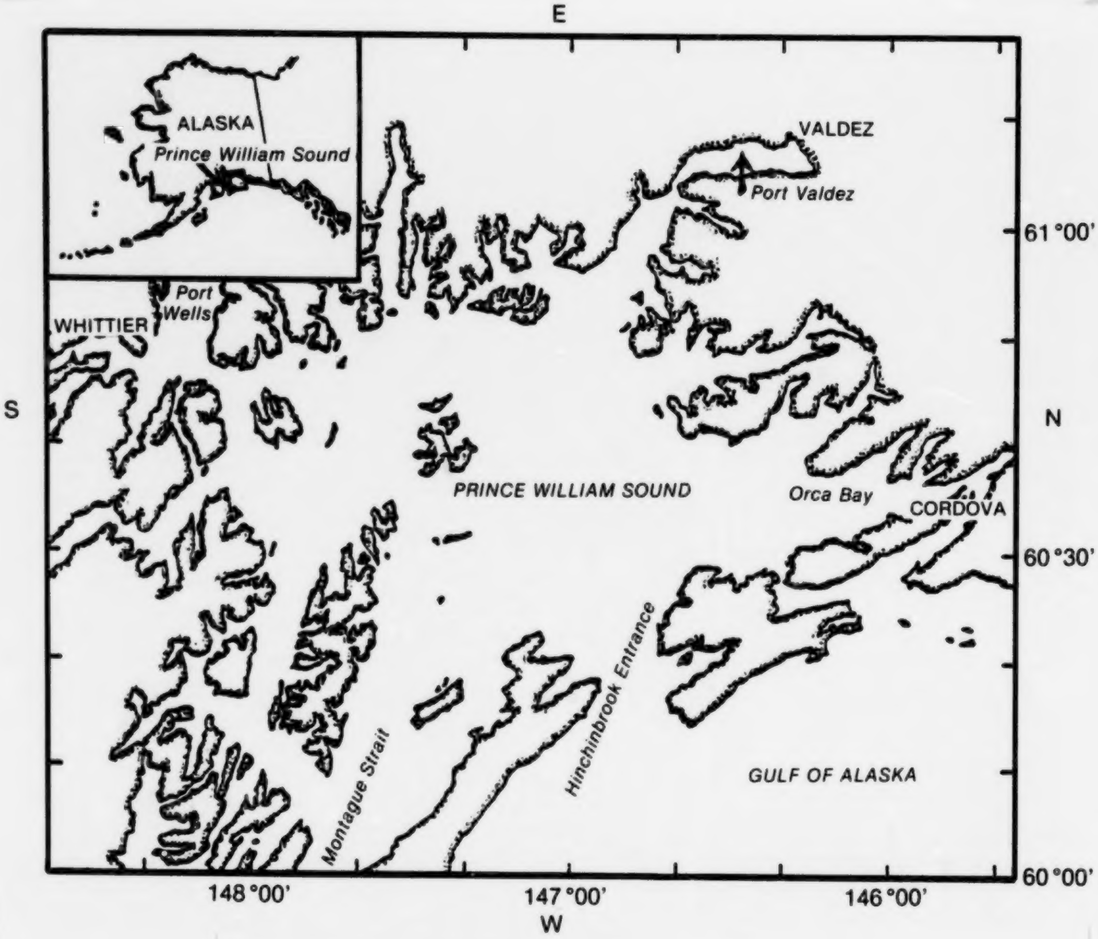
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Figure 1. Location of Port Valdez

METHODS

Analytical Methodology

Objectives of this study included determination of the effectiveness of removal of organic matter in a modern oily wastewater treatment operation and characterization of compositional changes in a process stream. To accomplish those objectives, it was necessary to monitor the organic content of the process stream in terms of the total material balance.

Preliminary tests were carried out on samples of process water from the Alyeska ballast treatment plant using the "Analytical Scheme for Analysis of Oily Wastewaters" (7). The analysis disclosed that organic matter present in the process stream included: volatile organic matter (lower molecular weight [MW] hydrocarbons), dissolved nonvolatile organic matter (including phenolic and naphthalenic compounds), and suspended oil. In order to develop information on the effectiveness of oil removal and to characterize the chemical redistribution taking place in the process, it was necessary to measure the concentrations of each organic fraction and to characterize chemically the principal compounds present.

To do so, an analytical protocol (7) was devised that included:

1. Determination and chemical characterization of volatile fraction
2. Determination and chemical characterization of dissolved nonvolatile fraction
3. Determination of suspended organic matter

In order to define overall organic concentration in the process stream, the Total Organic Load (TOL) was established. This corresponds to the sum of the volatile organics, dissolved nonvolatile organic matter, and suspended organic materials. The TOL value is expressed in mgC/L. The value of volatile hydrocarbons (which were determined as mg hydrocarbons/liter) was converted to mgC/L expression. Proportions of carbon to hydrogen in the principal hydrocarbons found (benzene, toluene, and xylenes) were used to calculate mg C/L values. Values for dissolved nonvolatile organics and for suspended organic matter were determined as mgC/L, and added to the converted values of volatile hydrocarbons. All TOL values reported here were so calculated.

Analysis of Volatile Fraction--

The volatile fraction of the process stream was composed largely of lower aromatic hydrocarbons (benzene, toluene, and xylenes). Some lower aliphatic hydrocarbons were present in the effluent from the gravity separator. Gas chromatographic procedure was used for analysis of this fraction.

A water sample (850 to 1000 milliliters [ml]) was sparged by the nitrogen gas and volatile hydrocarbons were adsorbed in an activated charcoal cartridge. Adsorbed hydrocarbons were then dissolved into 1 ml of carbon disulfide, providing for an 850- to 1000-fold concentration of volatile organic matter. A sample of this concentrate was injected into a gas chromatograph, separated into discrete fractions, and quantified using a hydrogen flame ionization detector.

Using this method and a Gow-Mac gas chromatograph, the detection limit for individual hydrocarbons was estimated at 0.1 microgram/liter, or 0.1 ppb (parts per billion). The identities of eluting peaks were established using computerized gas chromatograph-mass spectrometer (GC-MS). The quantification was performed using either peak height or area measurements on gas chromatograms.

Analysis for Dissolved Nonvolatile Organic Compounds--

The suspended oil was separated from the dissolved organic matter by Millipore filtration using a 0.45-micron HA-type filter. Dissolved organics are operationally defined as those that pass through the 0.45-micron filter. A similar definition is used by the EPA for operational definition of soluble and insoluble metals (Federal Register, Tuesday, December 18, 1979, Part IV, pages 75031-75036). The acidified and sparged filtrate was used for determination of total organic carbon (TOC) using Standard Method 510 (8). It was found that dissolved nonvolatile organic fraction contained phenolic and naphthalenic compounds. The concentration of those materials was determined as follows:

Phenolic compounds were separated from water using an Amberlite XAD-7 column. The adsorbed material was eluted into 25 ml of methanol and analyzed by High-Pressure Liquid Chromatography (HPLC). The analysis was performed using reverse phase mode of operation on an ODS-2 type of column. A water-methanol mixture was the moving phase (30:70). A UV spectrometer at a 254-nanometer (nm) adsorption band was used for detection and quantification of phenolic compounds. Naphthalenic compounds were separated from water by liquid-liquid extraction into chloroform and also analyzed by HPLC. The analysis conditions were similar to the ones described above.

Determination of Suspended Organic Matter--

A 100-ml sample was acidified, sparged with nitrogen, and ultrasonated using a Braun-Sonic Model 1510 probe at 300 watts power. The emulsified sample was injected into the TOC analyzer and total organic carbon was determined using Standard Method 510 (8). The suspended organic matter was determined as a difference between the concentration of total nonvolatile and dissolved organics. This fraction contained primarily aliphatic hydrocarbons of petroleum origin, and was not further chemically characterized. In addition, analyses for oil were performed for comparative purposes using Standard Methods 502A and 502B (8).

A detailed description of the analytical procedures used can be found in Appendix A.

Quality Control

The objective of quality control in analytical chemical work is to assure that generated data correctly reflect parameters of properly defined and accurately measured phenomena. This is done by eliminating false-positive and false-negative bias from the data and providing statistical validity in the accuracy and reproducibility of the reported data. The principal elements of a good quality control protocol are: instrumental and procedural blank determination, recovery data, multiple analysis of samples, daily multipoint calibration of instrumentation, statistical documentation of the accuracy and reproducibility of the methods used, and well-maintained documentation of all laboratory and sampling operations. A discussion of the key elements of quality control protocol utilized during the field and laboratory operations follows. A detailed description can be found in Appendix B.

Calibration--

Multipoint calibrations for n-hexane (model for aliphatic hydrocarbons), benzene, toluene, and xylenes were performed daily and new calibration graphs were prepared each day and used only during that day of operation. Multipoint calibration for TOC analysis was also performed daily using a potassium acid phthalate standard solution. The infrared spectrometer was calibrated daily

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in a similar manner using a mixture of benzene, isooctane, and n-hexadecane as specified in Standard Method 502B (8). Comparisons of daily calibration curves were made to detect any differences and/or drift in instrumental responses and/or changes in the composition of standard solutions.

Replicates--

All analyses were performed in triplicate, within a specified reproducibility range. Mean values are reported in the text of this report.

Contamination Check--

To assure the absence of contributions from the sample matrix and solvents, determinations of blank values were carried out daily on the gas chromatograph, TOC analyzer, and infrared spectrometer. The values for blanks were compensated for in the calculation of results.

Recovery--

Recovery studies were conducted for all chemical compounds that required separation from the water matrix as a part of the analytical procedure. Model chemical compounds were introduced in known quantities in 850-ml water samples and then analyzed in a manner identical to real samples. Recovery values were established for benzene, toluene, xylenes, phenols, and naphthalenic compounds.

Accuracy and Reproducibility--

Accuracy and reproducibility of all procedures used were established either from the literature (for standard methods) or determined experimentally for research procedures developed under this program. Details are reported in Appendix B.

TERMINAL BALLAST TREATMENT FACILITY IN PORT VALDEZ, ALASKA

The terminal ballast treatment facility in Port Valdez, Alaska, was designed by Incon, Inc., Engineers and Constructors, Houston, Texas. It was put into operation in August 1977 for continuously treating ballast waters from arriving tankers. The average rate of ballast treatment during the first year of operation was 40 million liters a day. The operational history of the plant is described in Appendix C. Following is a brief description of the original plant design, operational history, and plant modifications.

Original Plant Design

The Port Valdez terminal facility (Figure 2) utilizes primary treatment by gravity separation under quiescent aging conditions in aboveground and steel-cone-roof storage tanks, followed by a secondary treatment consisting of a chemically aided flocculation and a dissolved air flotation process (with capability for a final pH adjustment) and an effluent impound basin. Final disposal of the treated water is through a diffuser line laid into Port Valdez. Ballast water is discharged on-shore from arriving tankers through 1.07-meter-diameter pipes into holding tanks of 68,357-cubic-meter (m^3) (430,000-barrel) capacity. Gravity separation of oil from water takes place in those tanks over a period of 6 to 8 hours. Separated oil is recovered and reused. Each of the holding tanks has been sized and equipped to receive the entire ballast load from a 250,000-dead-weight-ton (dwt) tanker in 6 hours,

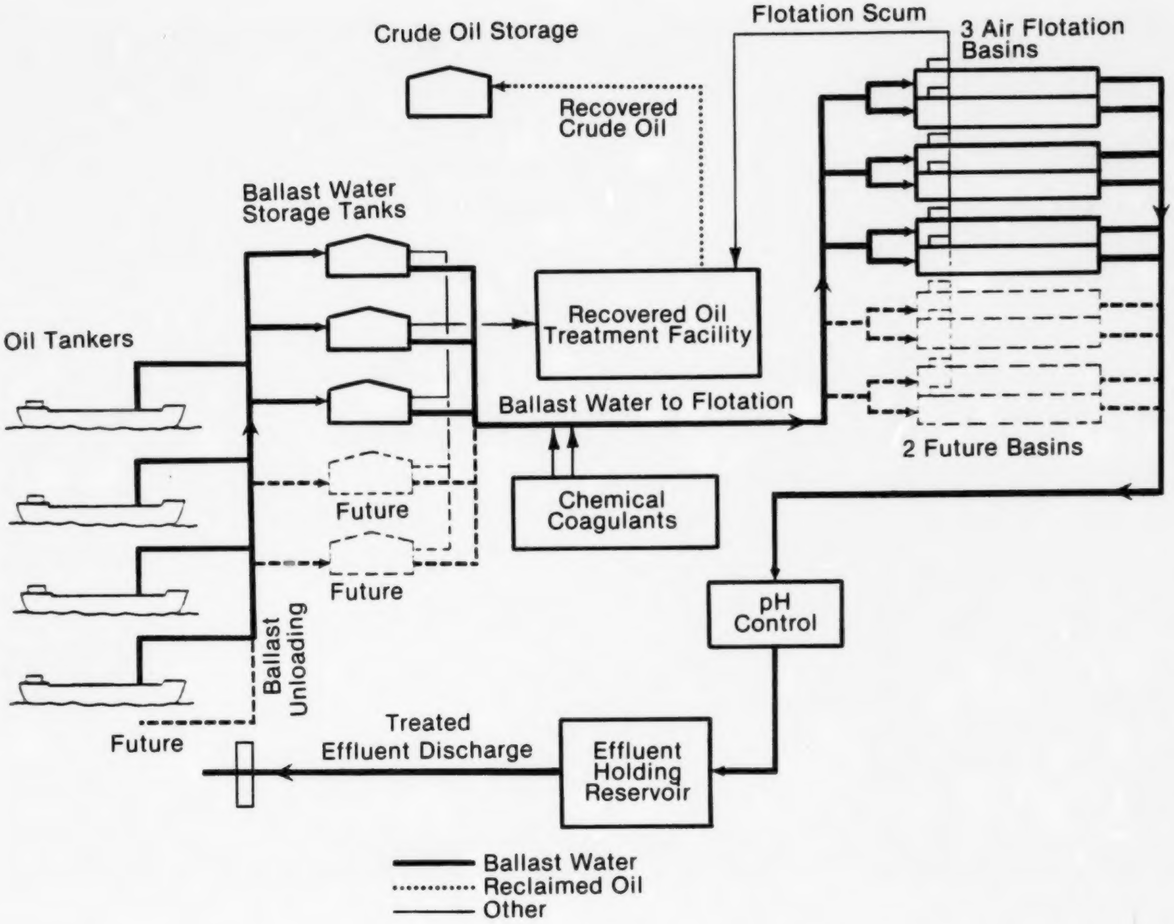
Crude Oil Storage
Flotation Scum
3 Air Flotation Basins
Recovered Crude Oil
Ballast Water Storage Tanks
Oil Tankers
Recovered Oil Treatment Facility
Ballast Water to Flotation
2 Future Basins
Future
Future
Chemical Coagulants
Ballast Unloading
pH Control
Future
Treated Effluent Discharge
Effluent Holding Reservoir
Ballast Water
Reclaimed Oil
Other

Figure 2. Ballast water treatment plant block diagram.

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and to hold the ballast for a minimum of 6 hours of quiescent aging before skimming and transfer of ballast begins.

The effluent from the gravity separators enters into a secondary aeration-flotation process unit. This system is an effluent recirculation kind where a side stream of treated water is pressurized, aerated, and mixed with wastewater undergoing treatment. In the aeration system, air is dissolved under pressure in the side stream and the liquid becomes supersaturated. As the pressure is released, the excess air comes out of solution in the form of minute bubbles. These bubbles collide with any suspended solids or oil globules in the stream and become attached. This changes the net specific gravity of the agglomerates, causing them to float. The floating particulate matter and oil are skimmed from the surface. The separation of oil from water by aeration is aided by the addition of flocculating chemical agents (alum and polyelectrolytes). The effluent from the secondary treatment unit enters holding ponds prior to discharge in the receiving waters of Port Valdez. The processing elements are sized for treating the entire contents of the primary separation and storage tanks within a 36-hour period, while effluent impounding facilities are sized to hold the initial average flow for a mean time of approximately 10 hours before its discharge into Port Valdez waters.

Operational History

The ballast water treating facility at the Alyeska Pipeline Service Company Marine Terminal in Port Valdez began operations in August 1977. Initially, an alum solution and a polyelectrol coagulant aid were injected into water drawn from the storage tanks. The process was designed to produce an alum floc in each of six flocculation chambers.

Shortly after the treatment plant started up, solids began forming in the impound basins in the form of settleable solids, a floating scum, and suspended solids. Plant personnel had to skim the surface of the basin with a vacuum truck daily, and periodically draw down a basin and remove the settled solids with fire hoses. These solids were recycled back into the treatment process.

In late 1977 a program was initiated at the terminal to determine the cause of solids in the impound basins and to find a method of preventing their occurrence. Samples of effluent from the the flotation chambers showed that floc formation was very poor and the floc observed was at best a finely divided microfloc. Efforts to produce a stronger floc that would form more rapidly were unsuccessful. A series of tests were conducted in which three pairs of flocculation and flotation chambers were isolated. Water passing through each pair of chambers was treated in a different manner. One pair of chambers was treated with alum and polyelectrolyte, a second pair was treated with a demulsifier, and the third pair received no chemical treatment.

As a result of these tests, in late 1978 the use of alum and polyelectrolyte was stopped and the plant switched to using a demulsifier only. The use of this product has greatly reduced the solids inventory that was building up in the system.

In addition to the problem with post-flocculation in the impound basins, the treatment plant began receiving some ballast water containing hydrogen sulfide in late 1977. To eliminate the problem of hydrogen sulfide gas in the flotation building, Alyeska began a program of treating ballast containing hydrogen sulfide with hydrogen peroxide. The hydrogen peroxide rapidly oxidizes hydrogen sulfide to free sulfur and water. Soon after the problem was identified, terminal personnel built a temporary hydrogen perioxide injection system between the ballast water storage tanks and the dissolved air flotation system. This temporary solution eliminated the problem of hydrogen sulfide gas in the flotation basin, but did not deal with the possible formation of the oil/water emulsion in the storage tanks. To prevent a buildup of sulfate-reducing bacteria in the storage tanks, a permanent hydrogen peroxide injection system was installed at the west manifold building of the terminal. This system treats ballast water from the ships prior to reaching the storage tanks.

FIELD STUDIES

The studies were carried out in Summer 1978, Winter 1979, and again in Summer 1979. During the first study period (August 1978), the treatment plant operated under conditions as originally designed, and the alum-electrolyte method of treatment was used in the dissolved aeration-flotation unit. Winter and Summer 1979 studies were carried out under modified conditions of plant operation when a demulsifier and hydrogen peroxide were used in the treatment process.

A detailed description of accumulated data is presented in Appendix D. Following is a brief description of results.

Summer 1978 Study

The first summer study was carried out during August 7-18, 1978. During this period the chemical composition of the final effluent was characterized on 10 consecutive days (August 7-16) and the primary effluent from the gravity separator was characterized on two consecutive days (August 17-18). The plant discharge rate ranged between 15,000 and 80,000 m^3/day, averaging 49,000 m^3/day. Water temperature ranged between 16.1 and 17.8°C, averaging 17.1°C.

The following analytical chemical operations were performed daily in the Valdez laboratory:

1. Determination of volatile hydrocarbon content, including concentrations of benzene, toluene, xylenes, and ethylbenzene

2. Determination of dissolved nonvolatile organic content

3. Determination of suspended nonvolatile organic content

4. Chloroform extraction for subsequent analysis of higher aromatic and polynuclear aromatic compounds

5. Macroreticular resin column (Amberlite XAD-7) separation for subsequent determination of phenolic content

Additionally, analyses for the total oil were carried out daily using Standard Methods 502A and 502B (8). Those analyses were performed for comparative purposes.

During the month of August 1978 the treatment plant processed 1.569 million m^3 of ballast water and recovered approximately 18,925 m^3 of oil from it. From this it can be calculated that the organic load of incoming untreated ballast water was at least 12,000 ppm. This concentration was reduced by the primary treatment in a gravity separator to approximately 20 mgC/L and then to approximately 11 mgC/L by the secondary treatment of aeration-flotation and holding tank retention. This corresponds to organic load reduction of 99.8% in the primary (gravity) separator, and 0.1% by the secondary treatment of aeration-flotation and holding tank retention.

The chemical composition of the effluent from the gravity separator is reported in Table 1. By far the largest organic fraction (60%) in the gravity separator effluent was composed of volatile hydrocarbons. This fraction was

TABLE 1. CHEMICAL COMPOSITION OF EFFLUENT FROM GRAVITY SEPARATOR, SUMMARY, AUGUST 17-18, 1978

	2-Day Average (mg/C/L)	Percent
1. Volatile Hydrocarbons		
Benzene	3.6	18
Toluene	3.0	15
Xylenes	1.6	8
Other	3.7	19
Total	11.9	60
2. Dissolved Nonvolatile Organics		
Phenolic Compounds	0.3	2
Naphthalenes and Derivatives	0.2	1
Other	2.5	13
Total	3.0	16
3. Suspended Nonvolatile Organics	4.7	24
TOTAL ORGANIC LOAD (TOL)	19.6	100

composed of aromatic hydrocarbons (8.2 mgC/L, or approximately 42% of the total organic load in the effluent), aliphatic hydrocarbons (3.7 mgC/L, or approximately 19% of the total organic load), and dissolved nonvolatile organic compounds (3.0 mgC/L, or approximately 16% of the total organic load). Phenolic compounds were present in 0.3-mgC/L concentrations (2% of the total organic load), and naphthalenes in 0.2-mgC/L concentrations (1% of the total organic load). The aromatic hydrocarbons were composed largely of benzene (3.6 mgC/L), toluene (3.0 mgC/L), and xylenes/ethylbenzene (1.6 mgC/L).

The chemical composition of the final effluent is reported in Table 2 and the range of concentrations in the final effluent is presented in Table 3. Examination of this data reveals that volatile hydrocarbons, which were composed mainly of aromatic hydrocarbons (benzene, toluene, and xylenes), constituted the largest and most significant component of organic composition in the treated effluent. Those three types of aromatic hydrocarbons constituted almost one-half of all organic matter present, with benzene and toluene contributing approximately one-fifth of the TOL each.

TABLE 2. CHEMICAL COMPOSITION OF FINAL EFFLUENT, SUMMARY, AUGUST 7-16, 1978

	10-Day Average (mgC/L)	Confidence Interval (E) (95%)	Percent
1. Volatile Hydrocarbons			
Benzene	2.3	± 0.5	21
Toluene	1.9	± 0.3	18
Xylenes	1.0	± 0.2	9
Other	0	-	-
Total	5.2	± 0.8	48
2. Dissolved Nonvolatile Organics			
Phenolic Compounds	0.4	± 0.15	4
Naphthalene and Alkyl Naphthalenes	0.24	± 0.03	2
Other	3.06	-	28
Total	3.7	± 0.4	34
3. Suspended Nonvolatile Organics	1.9	± 1.2	18
TOTAL ORGANIC LOAD (TOL)	10.8	± 2.4	100

TABLE 3. RANGE OF CONCENTRATIONS IN THE FINAL EFFLUENT, AUGUST 7-16, 1978

	mgC/L		
	Low	High	Mean
1. Volatile Hydrocarbons			
Benzene	1.3	3.5	2.4
Toluene	1.3	2.5	1.9
Xylenes/Ethylbenzene	0.6	1.4	1.0
Total	3.4	6.9	5.2
2. Nonvolatile Dissolved Organics	2.6	4.5	3.6
3. Suspended Organic Matter	0	3.5	1.9
TOTAL ORGANIC LOAD	7.7	13.4	10.6

The second important group of organics found in the final effluent were dissolved nonvolatile organics, which constituted about 34% of the TOL in the final effluent. Toxicologically important compounds in this group were phenolic compounds, found on an average at 0.4 mgC/L. They constituted approximately 4% of the TOL. Naphthalenic compounds were found on average at 0.24 mgC/L, and constituted approximately 2% of the TOL. Suspended nonvolatile organic matter was found to be the smallest component of organic composition in the final effluent. It contributed on the average only 18% to the TOL, and its concentration fluctuated between 0 and 3.5 mgC/L. This organic fraction was composed primarily of nonvolatile hydrocarbons and other water-insoluble, nonvolatile organic compounds. Such a composition falls under the traditional definition of "the oil," and is the principal component of the majority of crude oils. A very low level of this fraction was found in the treated effluent, testifying to the high efficiency and effectiveness of its removal by the ballast treatment plant.

During the period beginning August 7 through 16, 1978, the rate of effluent discharge fluctuated significantly (from 7.57 to 71.9 m^3/minute). The level of TOL in the final effluent, however, was relatively stable, with a low of 7.7 mgC/L and a high of 13.4 mgC/L. This represented 72% to 125% fluctuation from the mean value, and indicated that the plant was handling wide-ranging volumes of ballast reasonably well.

The fluctuation in concentration of dissolved nonvolatile organic matter was similar to that of TOL, covering a range of 70% to 120% of mean value. Aromatic hydrocarbon fluctuation was somewhat greater, and covered the range of 66% to 136%. The concentration of suspended organic matter fluctuated from nil to 200% of the mean value.

The data on reduction of the organic content of the process stream resulting from dissolved aeration-flotation treatment is presented in Table 4. Examination of this table indicates that the secondary treatment reduces by approximately 60% suspended organic matter and by 56% volatile hydrocarbons. Volatile aliphatic hydrocarbons are eliminated totally, while volatile aromatic hydrocarbon content is reduced by approximately 37%.

As expected, the secondary treatment did not reduce dissolved nonvolatile organic content of the stream.

Winter 1979 Study

The winter study was carried out during the February 19 through March 2 time period. The plant was operating at this time under different conditions from the previous summer study. Instead of the alum-electrolyte treatment that was used in August 1978, demulsifiers and hydrogen peroxide were used as a part of the treatment. The other significant difference between Summer 1978 and Winter 1979 plant operation was the volume of ballast water processed. The average discharge rate observed during the 12 days of the August 1978 study was 49,205 m^3 per day, while the average for 10 days of the Winter 1979

TABLE 4. REDUCTION OF ORGANIC CONTENT IN PROCESS WATER BY THE SECONDARY* TREATMENT PROCESS, PORT VALDEZ, ALASKA, AUGUST 7-18, 1978

	Gravity Separator Effluent (mgC/L)	Effluent (mgC/L)	Reduction by Secondary Treatment* (%)
Suspended Organic Matter (Free Oil)	4.7	1.9	60
Dissolved, Nonvolatile Organic Matter	3.0	3.7	0
Volatile Hydrocarbons			
Benzene	3.6	2.3	36
Toluene	3.0	1.9	37
Xylenes/Ethylbenzene	1.6	1.0	38
Other Hydrocarbons	3.7	0	100
Total Volatile Hydrocarbons	11.9	5.2	56
TOTAL ORGANIC LOAD	19.6	10.8	45

* Dissolved aeration-flotation.

operation was 90,840 m^3 per day, or almost double the summer rate. The weather was the principal reason for higher rates of ballast processing in the winter. In order to compensate for heavier seas during winter months, tankers were loaded with more ballast water. Additionally, just prior to initiation of the Winter 1979 study, violent winds stopped all oil tanker traffic in Port Valdez for a numberof days and curtailed the terminal loading operation. The terminal operations were renewed during our study period and, in order to unload excess oil from the storage tanks, the plant was operating near its full capacity.

The plant average discharge during this period was 90,840 m^3 per day and average water temperatures were as follows: incoming ballast, 6.6°C, primary effluent, 8.0°C, final effluent, 9.2°C.

During this work period an attempt was made to monitor changes in the chemical composition of the process stream starting with incoming ballast from a given tanker and continuing through the primary process of gravity separation and the secondary process of aeration-flotation and holding pond retention. To do so, it was necessary to synchronize the sampling sequence with the process stream flow. The sampling sequence was normally initiated with the arrival of a tanker on a given day. Records of plant operation and flowrates were then consulted and the passage of ballast through the treatment system was closely followed. The water samples were collected at the various points of the process stream at times calculated from prevailing flowrates for that day.

This scheme required continuous, around-the-clock sampling. Assistance from Alyeska Pipeline Service Company personnel in carrying out the sampling operation was essential to the success of the Winter 1979 study. On the average, three sets of samples (incoming ballast, primary effluent from the gravity separator, and the final treated effluent) were collected each day and analyzed for:

1. Volatile hydrocarbon content, including aliphatics, benzene, toluene, xylenes, and ethylbenzene,
2. Dissolved nonvolatile organic content, and
3. Suspended organic matter.

Representative sampling of incoming ballast from the tankers proved to be rather difficult. The chemical composition of ballast water within holds of tankers varied in the vertical plane with higher concentrations of suspended oil near the surface and the lower concentration of suspended oil near the bottom of tanker compartments.

Because of variances of values for suspended oil in the stream of incoming untreated ballast water, its concentration was estimated from plant operating records. The estimate of suspended oil content in the incoming ballast water was based on engineering process data: amount of oil recovered by the treatment plant and volume of ballast processed. The experimental data provided information on volatile and dissolved nonvolatile organic content. TOL value in the incoming untreated ballast was then estimated from experimental data and plant operating records.

During the month of February 1979 the treatment plant processed 1.752 million m^3 of ballast water from which approximately 12,869 m^3 of oil were recovered. From this it can be calculated that the oil content of incoming ballast water was, on the average, at least 7300 ppm. The volatile hydrocarbons and dissolved nonvolatile organics added approximately 20 mgC/L to this value. This concentration was reduced, by primary treatment in the gravity separator, to approximately 16 mgC/L and then to approximately 11 mgC/L by secondary treatment of aeration-flotation and holding tank retention. This corresponds to an organic load reductidon of 99.8% in the primary separator, and 0.1% from secondary treatment. The overall plant effectiveness in removal of the oil from the ballast water was found to be 99.9%.

The summary of combined data (deduced and experimental) on the chemical composition of untreated ballast is shown in Table 5. In preparing this table, it was assumed that the bulk of volatile aromatic hydrocarbons are present in aqueous fraction. This is because lower aromatic hydrocarbons are quite soluble in water (benzene, 1780 mg/liter at 20°C; toluene, 515 mg/liter at 20°C; and xylenes, 198 mg/liter at 25°C) and the ratio of water to oil (10,000:1) would favor such distribution. Examination of this table reveals that suspended oil (removable by means of physical separation) is by far the largest fraction of organic load in untreated ballast (approximately 7300 ppm). Dissolved organic fraction amounts to only 5 mgC/L, and volatile hydrocarbons (aromatic and aliphatic) amounted to approximately 13 mgC/L.

The effluent from the gravity separator was examined on 10 consecutive days and the summary of results is presented in Table 6. The range of concentrations observed is reported in Table 7. Examination of this data reveals that the total organic load of the primary effluent was approximately 16 mgC/L. Volatile hydrocarbons comprised the largest single fraction of the total organic load (45%), followed by the dissolved nonvolatile fraction (34%) and suspended organic matter (21%). Benzene, toluene, and xylenes/ethylbenzene

TABLE 5. CHEMICAL COMPOSITION OF UNTREATED BALLAST, SUMMARY, FEBRUARY 19 - MARCH 2, 1979

	10-Day Average (mgC/L)	Confidence Interval (E) (95%)	Percent
1. Volatile Hydrocarbons			
Benzene	3.5	± 0.9	0.05
Toluene	3.1	± 0.9	0.04
Xylenes/Ethylbenzene	2.0	± 0.4	0.03
Other	4.4	± 0.9	0.06
Total	13.0	± 2.3	0.2
2. Dissolved Nonvolatile Organics	4.9	± 2.6	0.1
3. Suspended Oil (estimated)	∿7300		99.7
TOTAL ORGANIC LOAD (ESTIMATED)	∿7320		100

TABLE 6. CHEMICAL COMPOSITION IN EFFLUENT FROM GRAVITY SEPARATOR, SUMMARY, FEBRUARY 19 - MARCH 2, 1979

	10-Day Average (mgC/L)	Confidence Interval (E) (95%)	Percent
1. Volatile Hydrocarbons			
Benzene	2.6	± 0.4	16
Toluene	2.4	± 0.3	15
Xylenes/Ethylbenzene	1.3	± 0.1	8
Other	1.0	± 0.2	6
Total	7.3	± 0.9	45
2. Dissolved Nonvolatile Organics	5.4	± 0.9	34
3. Suspended Nonvolatile Organics	3.4	± 1.6	21
TOTAL ORGANIC LOAD	16.1	± 2.0	100

TABLE 7. RANGE OF CONCENTRATIONS IN THE PRIMARY EFFLUENT, FEBRUARY 19 - MARCH 2, 1979

	mgC/L		
	Low	High	Mean
1. Volatile Hydrocarbons			
Benzene	1.2	3.5	2.4
Toluene	1.3	3.0	2.2
Xylenes/Ethylbenzene	0.8	1.7	1.3
Other	0.5	1.7	1.2
Total	7.8	3.9	5.9
2. Dissolved Nonvolatile Organics	8.0	3.2	5.6
3. Suspended Organics	7.4	0.1	3.8
TOTAL ORGANIC LOAD	22.6	8.0	15.3

were the principal individual hydrocarbons present in the effluent. The TOL values in the primary effluent fluctuated between 52% and 148% from mean value. The values for individual fraction fluctuations were: volatile hydrocarbons, 66% to 132%; dissolved nonvolatile organics, 57% to 143%; suspended nonvolatile organics, 3% to 195%.

A summary of the data on the chemical composition of the final effluent is given in Table 8 and the range of concentrations observed is presented in Table 9. Examination of this data reveals remarkable similarity to the chemical composition observed during the Summer 1978 study. This similarity is

TABLE 8. CHEMICAL COMPOSITION OF FINAL EFFLUENT, SUMMARY, FEBRUARY 19 - MARCH 2, 1979

	10-Day Average (mgC/L)	Confidence Interval (E) (95%)	Percent
1. Volatile Hydrocarbons			
Benzene	1.9	± 0.5	17
Toluene	1.8	± 0.3	17
Xylenes/Ethylbenzene	0.9	± 0.1	8
Other	0.2	± 0.06	2
Total	4.8	± 0.7	44
2. Dissolved Nonvolatile Organics	5.2	± 0.3	48
3. Suspended Nonvolatile Organics	0.9	± 0.8	8
TOTAL ORGANIC LOAD	10.9	± 0.9	100

TABLE 9. RANGE OF CONCENTRATIONS IN FINAL EFFLUENT, SUMMARY, FEBRUARY 19 - MARCH 2, 1979

	mgC/L		
	Low	High	Mean
1. Volatile Hydrocarbons			
Benzene	1.2	2.9	2.1
Toluene	1.1	2.4	1.8
Xylenes/Ethylbenzene	0.5	1.1	0.8
Other	0.1	0.5	0.3
Total	2.9	6.8	4.9
2. Dissolved Nonvolatile Organics	4.5	5.8	5.2
3. Suspended Organic Matter	-	3.2	1.6
TOTAL ORGANIC LOAD	7.7	15.8	11.7

rather remarkable, considering that day-to-day fluctuations in all parameters studied were of a significant degree as expressed in high and low values measured and confidence intervals calculated.

Total organic load values were found to be 10.8 mgC/L in the Summer 1978 study and 10.9 mgC/L in the Winter 1979 study. Aromatic hydrocarbons constituted 48% of TOL value in the summer study and 44% of TOL value in the winter study. The reported data indicates that aromatic hydrocarbons (composed primarily of benzene, toluene, and xylenes/ethylbenzene) constituted by far the largest and most important class of organic materials detected. The notable presence of small amounts of volatile aliphatic hydrocarbons in the final effluent (0.2 mgC/L) suggests less efficient removal of this material by the secondary aeration-flotation during winter months when the process water was lower in temperature. Volatile aliphatic hydrocarbons were totally eliminated in the summer study by the secondary process.

The dissolved organic content was found to average 5.2 mgC/L in the Winter 1979 study, as opposed to 3.7 mgC/L found on the average during the Summer 1978 study. Suspended nonvolatile organics, however, were found in lower concentrations (0.9 mgC/L) in the winter study, as compared with 1.9 mgC/L found in the Summer 1978 study. This improvement in removal of suspended organic matter during the winter study might be because of the change in operating conditions, i.e., substitution of the demulsifier treatment for alum-electrolyte treatment in the aeration-flotation operation.

During the Winter 1979 study the treatment plant was operating near its full capacity with little fluctuation in flowrates. The fluctuations in chemical composition on different days were similar, however, to the Summer 1978 study when plant flowrates varied widely.

The TOL values in the final effluent fluctuated between 56% and 139% of mean value. The fluctuation in volatile hydrocarbon content was in a similar range (59% to 139%). The fluctuation in dissolved organic content was somewhat narrower (86% to 111%). The suspended organic matter ranged from 0% to 200% of mean value.

Reduction in organic content of the process stream observed during the Winter 1979 study is reported in Table 10. Examination of this table indicates that the bulk of suspended oil is removed by the gravity separator. The gravity separator also reduced volatile hydrocarbon content of the untreated ballast water by 44% and aliphatic hydrocarbon by 77%. Additional reductions of volatile hydrocarbons are effected in the dissolved aeration-flotation operation. The treatment process, however, did not reduce the concentration of dissolved nonvolatile fraction.

Summer 1979 Study

The second summer study was carried out during the June 19-30, 1979, time period. The plant was operating at this time under modified conditions: a demulsifier was used in the aeration-flotation process rather than an alum-electrolyte mix. The average rate of discharge for 10 days of the study period was 49,205 m^3/day. This value was the same as reported during the first summer study in 1978. The average water temperatures were: effluent gravity separator, 15°C, final effluent, 17°C. The primary effluent from the gravity separator and the final treated effluents were collected. The sampling scheme was synchronized with plant flowrates in such a way that each data set could be related to ballast discharge from a given tanker.

Two sets of samples were collected for each operational sequence and analyzed for:

TABLE 10. STEPWISE REDUCTION OF ORGANIC CONTENT IN PROCESS WATER BY THE TREATMENT PROCESS, FEBRUARY 19 - MARCH 2, 1979

	Untreated Ballast (mgC/L)	Reduced by (%)	Gravity Separator Effluent (mgC/L)	Reduced by (%)	Final Effluent (mgC/L)	Total Reduction by the Process (%)
1. Volatile Hydrocarbons						
Benzene	3.5	26	2.6	27	1.9	46
Toluene	3.1	23	2.4	25	1.8	42
Xylenes/Ethylbenzene	2.0	35	1.3	31	0.9	55
Other	4.4	77	1.0	80	0.2	96
Total	13.0	44	7.3	34	4.8	63
2. Suspended Organic Matter	~7300*	99.95	3.4	74	0.9	99.99
3. Dissolved Nonvolatile Organic Matter	4.9	0	5.4	4	5.2	0
TOTAL ORGANIC LOAD	~7320	99.8	16.1	32	10.9	99.9

* Estimated from plant production figures for February 1979.

1. Volatile hydrocarbon content, including aliphatic hydrocarbons, benzene, toluene, xylenes, and ethylbenzene

2. Nonvolatile dissolved organic content

3. Suspended organic matter

During the month of June 1979 the treatment plant processed 1.049 million m^3 of ballast water and recovered approximately 10,977 m^3 of the oil. From this it can be calculated that the organic load of the incoming ballast was at least 10,000 ppm. This concentration was reduced by primary treatment in the gravity separator to approximately 16 mgC/L and then to approximately 10 mgC/L by the secondary treatment of aeration-flotation and holding tank retention. This corresponds to an organic load reduction of 99.8% in the primary separator and 0.1% in the secondary treatment. The overall effectiveness of the treatment plant in removal of the oil from the ballast water was found to be 99.9%. The plant performance in June 1979 closely matched plant performance in February-March 1979 and August 1978. This suggests that there are no significant seasonal effects on plant operation, and that overall plant performance is remarkably consistent.

The effluent from the gravity separator was examined during the 11 days of the second summer study and the results are presented in Table 11. Examination of this data reveals that the total organic load of the primary effluent was approximately 16 mgC/L, duplicating exactly the total organic load in the primary separator observed during the preceding winter (February 1979) study. Volatile hydrocarbons comprised the largest single fraction of the total organic load (55%), followed by dissolved nonvolatile fraction (28%) and suspended organic matter (17%). Benzene, toluene, and xylenes/ethylbenzene were the principal individual hydrocarbons present in the effluent. The TOL values in the primary effluent fluctuated between 64% and 136%. The values for individual fraction fluctuations (Table 12) were:

Volatile Hydrocarbons	59% to 141%
Dissolved Nonvolatile Organics	36% to 162%
Suspended Nonvolatile Organics	27% to 171%

A summary of generated data on the chemical composition of the final effluent is reported in Table 13, and the range of concentrations observed is presented in Table 14. Examination of this data reveals a remarkable similarity between chemical compositions of final effluent observed during two summer studies and one winter study in Port Valdez, Alaska. It must be stated again that this remarkable similarity in 10-day average values for all study periods is in spite of wide day-to-day variations in every parameter measured. Total average (10 day) organic load values for the final effluent were found to be 10.8 mgC/L in the summer (August 1978) study, 10.9 mgC/L during the winter (February 1979) study, and 10.2 mgC/L during the second summer study (June 1979).

Volatile hydrocarbons constituted 48% of the TOL during the first summer study (August 1978), and 44% during both Winter and Summer 1979 studies. The aromatic hydrocarbons (composed of benzene, toluene, and xylenes/ethylbenzene)

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TABLE 11. CHEMICAL COMPOSITION OF THE EFFLUENT FROM THE GRAVITY SEPARATOR, SUMMARY, JUNE 19-30, 1979

	11-Day Average (mgC/L)	Confidence Interval (E) (95%)	Percent
1. Volatile Hydrocarbons			
Benzene	3.0	± 0.4	19
Toluene	3.0	± 0.3	19
Xylenes/Ethylbenzene	1.3	± 0.1	8
Other	1.6	± 0.3	10
Total	8.9	± 1.5	55
2. Dissolved Nonvolatile Organics	4.5	± 1.6	28
3. Suspended Nonvolatile Organics	2.7	± 1.4	17
TOTAL ORGANIC LOAD	16.1	± 2.6	100

TABLE 12. RANGE OF CONCENTRATIONS IN THE GRAVITY SEPARATOR EFFLUENT, JUNE 19-30, 1979

	mgC/L		
	High	Low	Mean
1. Volatile Hydrocarbons			
Benzene	5.0	1.3	3.2
Toluene	4.9	1.8	3.4
Xylenes/Ethylbenzene	1.6	0.7	1.2
Other	2.4	1.0	1.7
Total	13.1	5.5	9.3
2. Dissolved Nonvolatile Organics	9.4	2.1	5.8
3. Suspended Nonvolatile Organics	7.0	1.1	4.1
TOTAL ORGANIC LOAD	23.5	11.1	17.3

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TABLE 13. CHEMICAL COMPOSITION OF THE FINAL EFFLUENT, SUMMARY, JUNE 19-30, 1979

	11-Day Average (mgC/L)	Confidence Interval (E) (95%)	Percent
1. Volatile Hydrocarbons			
Benzene	1.8	± 0.4	18
Toluene	1.7	± 0.3	17
Xylenes/Ethylbenzene	0.7	± 0.1	7
Other	0.2	± 0.05	2
Total	4.4	± 0.8	43
2. Dissolved Nonvolatile Organics	3.9	± 0.8	38
3. Suspended Nonvolatile Organics	1.9	± 0.8	19
TOTAL ORGANIC LOAD	10.2	± 1.4	100

TABLE 14. RANGE OF CONCENTRATIONS IN THE FINAL EFFLUENT, SUMMARY, JUNE 19-30, 1979

	mgC/L		
	High	Low	Mean
1. Volatile Hydrocarbons			
Benzene	2.7	0.4	1.5
Toluene	2.4	0.5	1.5
Xylenes/Ethylbenzene	1.0	0.4	0.7
Other	0.4	0.1	0.3
Total	6.1	3.0	4.5
2. Dissolved Nonvolatile Organics	5.6	2.4	4.0
3. Suspended Nonvolatile Organics	4.0	1.1	2.6
TOTAL ORGANIC LOAD	14.6	6.2	10.4

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constituted the single largest fraction of organic material detected in the final effluent.

The TOL values in the final effluent fluctuated between 60% and 140% of mean value. The fluctuation of individual fractions was as follows:

Volatile Hydrocarbons	60% to 134%
Dissolved Nonvolatile Organics	60% to 140%
Suspended Nonvolatile Organics	12% to 154%

The reduction of organic load as a result of secondary treatment is reported in Table 15. Examination of this table indicates that the secondary treatment of aeration-flotation and impoundment reduces volatile hydrocarbons by approximately 50%, dissolved organic matter by 13%, and suspended organic matter by 30%, resulting in an averall 37% reduction of organic load in the effluent from the primary separator.

TABLE 15. REDUCTION OF ORGANIC CONTENT IN PROCESS WATER BY THE TREATMENT PROCESS, PORT VALDEZ, ALASKA, JUNE 19-30, 1979

	Gravity Separator Effluent (mgC/L)	Final Effluent* (mgC/L)	Reduction by the Secondary Process (%)
1. Volatile Hydrocarbons			
Benzene	3.0	1.8	40
Toluene	3.0	1.7	43
Xylenes/Ethylbenzene	1.3	0.7	38
Other	1.6	0.2	88
Total	8.9	4.4	50
2. Dissolved Nonvolatile Organic Matter	4.5	3.9	13
3. Suspended Organic Matter (Free Oil)	2.7	1.9	30
TOTAL ORGANIC LOAD	16.1	10.2	37

* Dissolved aeration-flotation.

RESULTS AND DISCUSSION

Treatment Plant Effectiveness

The effectiveness of oily wastewater treatment can be defined as its ability to remove petroleum and related organic matter from the water. Determination of organic load reduction in the process stream can be considered as a measure of process effectiveness.

The process stream in a ballast water treatment plant originates with untreated ballast incoming from arriving tankers and ends with treated effluent in the diffuser pipes laid on the bottom of Port Valdez. During the passage through the plant, ballast water undergoes two principal physical separations: quiescent gravity separation in primary holding tanks, and dissolved air flotation process in flowthrough chambers. Consequently, the chemical composition of the process water is expected to be qualitatively and quantitatively different at three major points in the process: incoming ballast, effluent from the gravity separator, and final treated effluent. Those three points were selected as the principal sampling points during this study.

The analysis of primary and final effluents conducted during study periods of Summer 1978, Winter 1979, and Summer 1979 indicated very little difference (qualitative or quantitative) in the average chemical composition of the process stream (from season to season), as shown in Table 16. The reason for this may lie in the averaging effect of the large volumes of water processed, consistency of plant operational procedures, and relative similarity in the chemical composition of incoming ballast water. For this reason, all the experimental data obtained during this study for primary and final effluent chemical composition was averaged and is used in this manner in subsequent discussions. Using this data, it was possible to develop complete organic material balances for the primary and the final effluents.

However, difficulties were experienced in representative sampling of incoming untreated ballast water. The ballast in tanker compartments is heterogeneous and oil and water are fairly well separated. This fact makes representative sampling of incoming water extremely difficult. The difficulty was overcome by combined use of plant operating records and the experimental data to produce organic material balance for incoming untreated ballast waters. The plant records contained information on the amount of water processed and the amount of free oil removed. Based on the 2 years of plant operation records, it was estimated that incoming ballast water contained an average of 7200 ppm of suspended (recoverable) oil. The concentration of dissolved organic matter (volatile and nonvolatile) in the incoming untreated ballast was determined during the 10 days of the Winter 1979 study. A combination of those two sources of data provided for organic material balance in the incoming ballast.

The 2-year average for suspended oil was estimated to be 7200 ppm, while the level of all dissolved organics was experimentally determined at approximately 20 mgC/L. Consequently, the total organic load of incoming untreated ballast is estimated at 7220 ppm. The dissolved organics were composed of approximately 13 mgC/L of volatile hydrocarbons and 5 mgC/L nonvolatile organic compounds. The organic load of incoming ballast was reduced to approximately

TABLE 16. COMPOSITIONS OF PRIMARY AND FINAL EFFLUENTS, VALDEZ, ALASKA BALLAST WATER TREATMENT PLANT, SUMMARY, AUGUST 1978 - JUNE 1979

	August 7-18, 1978		February 19-March 2, 1979		June 19-30, 1979		Average		Average %
	Primary	Final	Primary	Final	Primary	Final	Primary	Final	Reduction
Volatile Hydrocarbons									
Benzene	3.6	2.3	2.6	1.9	3.0	1.8	3.1	2.0	35
Toluene	3.0	1.9	2.4	1.8	3.0	1.7	2.8	1.8	36
Xylenes/ Ethylbenzene	1.6	1.0	1.3	0.9	1.3	0.7	1.4	0.9	35
Other	3.7	0	1.0	0.2	1.6	0.2	2.1	0.2	90
Total	11.9	5.2	7.3	4.8	8.9	4.4	9.2	4.9	47
Dissolved Nonvolatile Organics	3.0	3.7	5.4	5.2	4.5	3.9	4.3	4.3	0
Suspended Nonvolatile Organics	4.7	1.9	3.4	0.9	2.7	1.9	3.6	1.5	58
Total Nonvolatiles	7.7	5.6	8.8	6.1	7.2	5.8	7.9	5.8	27
TOTAL ORGANIC LOAD	19.6	10.8	16.1	10.9	16.1	10.2	17.3	10.6	39

All values are average of 10 days of plant operation expressed in mgC/L.

17 mgC/L by the gravity separator treatment and then was finally reduced to approximately 11 mgC/L by the secondary treatment of aeration-flotation and in-tank retention. The overall organic load reduction by the treatment plant was in the order of 99.8% to 99.9%, as shown in Table 17.

The elimination of suspended organic matter (the oil) was almost complete: 99.97% of it was removed by the process. The dissolved organic matter content was reduced by only 50%, with most of the reduction taking place in the volatile fraction (62%). The concentration of dissolved nonvolatile fraction was reduced by only 20%. The overall reduction of volatile hydrocarbons was approximately 62%, while reduction of volatile aliphatic hydrocarbons was almost complete (95%).

The gravity separator reduced total organic load by 99.8%, while the dissolved air flotation unit improved on this reduction by less than 0.1%.

The effectiveness of plant operation can be summarized in the following manner: the gravity separator removes the great bulk of suspended oil, and some of the dissolved organic compounds (both volatile and nonvolatile). The dissolved aeration-flotation operation contributes to further reduction of volatile organic matter, but has very little effect on the concentration of dissolved nonvolatile organics.

It must be kept in mind that dissolved aeration-flotation chambers are designed for removal of free oil rather than volatile hydrocarbons. Mild aeration is used to float oil particles with minimum agitation. The analytical procedure used for complete removal of volatile hydrocarbons is based on use of 15 liters of nitrogen per 1 liter of water under vigorous agitation conditions.

Compositional Changes in the Process Stream

The treatment process changed the chemical composition of the process stream quantitatively and qualitatively. Different fractions of organic matter present in the ballast water were removed at different rates by each operating step of the process. As a result, the chemical makeup of the final effluent was quite different from the chemical makeup of incoming untreated ballast water, as shown in Table 18.

Examination of this table indicates that the most drastic change in chemical composition of the process water took place in the gravity separator. Suspended organic matter (the oil), which contributed 99.7% to the organic load of untreated bilge, was reduced to only 21% of the organic load in the gravity separator effluent, and 14% in the final effluent. The proportion of dissolved organic matter (a sum of volatile and nonvolatile dissolved organics) increased dramatically from 0.3% in untreated ballast to 80% in the effluent from the primary separator and 86% in the final effluent. The aromatic hydrocarbon (benzene, toluene, xylenes) concentrations were measured in fractions of a percent in the untreated ballast water, but constituted almost one-half of all organic matter in the final effluent. The qualitative nature of the process stream downstream from the gravity separator was not changed significantly. For example, proportions of benzene, toluene, and xylenes/ethylbenzene

TABLE 17. STEPWISE REDUCTION OF ORGANIC CONTENT IN PROCESS WATER BY THE TREATMENT PROCESS, PORT VALDEZ, ALASKA, SUMMARY, AUGUST 1978 - JUNE 1979

	Untreated Ballast (mgC/L)	Reduced by (%)	Gravity Separator Effluent (mgC/L)	Reduced by (%)	Final Effluent (mgC/L)	Total Reduction by the Process (%)
1. Volatile Hydrocarbons						
Benzene	4	25	3	33	2	50
Toluene	3	0	3	33	2	33
Xylenes/Ethylbenzene	2	0	2	50	1	50
Other	4	50	2	90	0.2	95
Total	13	30	9	44	5	62
2. Dissolved Nonvolatile Organic Matter	5	20	4	0	4	20
3. Suspended Organic Matter (Free Oil)	~7200	99.9	4	50	2	99.97
TOTAL ORGANIC LOAD	~7220		17	35	11	99.8

TABLE 18. AVERAGE CHEMICAL COMPOSITIONAL CHANGES IN THE PROCESS STREAM

	Untreated Ballast		Gravity Separator Effluent		Final Effluent	
	Concentration (mgC/L)	%	Concentration (mgC/L)	%	Concentration (mgC/L)	%
Volatile Hydrocarbons						
Benzene	4	0.06	3.1	18	2.0	19
Toluene	3	0.04	2.8	16	1.8	17
Xylenes/ Ethylbenzene	2	0.03	1.4	8	0.9	8
Other	4	0.06	2.1	12	0.2	0.2
Total	13	0.2	9.4	54	4.9	46
Dissolved Nonvolatile Organic Matter	5	0.07	4.3	25	4.3	40
Suspended Organic Matter	∿7200	99.7	3.6	21	1.5	14
TOTAL ORGANIC LOAD	∿7220	100	17.3	100	10.7	100

were essentially the same in the effluent from the gravity separator and in the final effluent.

Significantly changed by the secondary treatment of aeration-flotation were concentrations and proportions of volatile aliphatic hydrocarbons, which were essentially eliminated in the secondary treatment. The concentration and proportion of suspended organic matter (the oil) were also reduced significantly by the secondary treatment.

Aromatic Hydrocarbons in the Process Stream and the Effluent

After the bulk of suspended oil was separated and removed by the gravity separator, aromatic hydrocarbons became the single largest component of the process stream. Benzene, toluene, xylenes, and ethylbenzene alone constituted approximately 40% to 50% of the total organic load in the effluent from the gravity separator and in the final treated effluent. The average (based on three seasonal studies) concentration level for aromatic hydrocarbons was found to be 9 mgC/L in the primary effluent and 5 mgC/L in the final effluent.

The volume of ballast water treated at the Port Valdez treatment plant is rather high. It averaged approximately 39,743 m^3 per day for the first year of plant operation, and rose steadily during the next year. During the first 3 months of operation in 1979, the average process rate rose to 56,775 m^3 per day. Because of this large volume of water discharged, it is worthwhile to examine the treated effluent not only in terms of organic concentration (mgC/L) but also in terms of absolute quantities of organic matter, including volatile aromatic hydrocarbons that are discharged into the receiving waters of Port Valdez. It was possible to calculate quantities of organic matter discharged daily in terms of liters using known discharge rates and analytical data reported previously. Such a computation was performed for each of the three study periods and the results are reported in Tables 19, 20, and 21.

During the first summer study in August 1978, the average daily discharge of organic matter was as follows: aromatic hydrocarbons, 273 liters (L), dissolved nonvolatile organics, 173 L, and suspended organic matter, 84 L. The discharge rates rose in winter, when larger volumes of ballast were processed. Daily averages during the Winter 1979 study were found to be: aromatic hydrocarbons, 462 L, dissolved nonvolatile organics, 471 L, suspended organic matter, 86 L.

During the second summer study in June 1979, organic discharge rates were similar to the rates recorded during the first summer study. Discharged daily in June 1979 were: aromatic hydrocarbons, 250 L, dissolved nonvolatile organics, 208 L, suspended organics, 91 L. It is interesting to note that while daily discharge volumes of aromatic hydrocarbons and dissolved nonvolatile organic matter fluctuated between winter and summer study periods, the volume of suspended organic matter discharged was fairly constant: August 1978, 84 L per day; February 1979, 86 L per day; and June 1979, 91 L per day. The information regarding discharge of aromatic hydrocarbons is summarized in Table 22.

Examination of this table reveals that similar amounts of ballast were processed during the Summer 1978 study (an average of 45,400 m^3 per day) and during the Summer 1979 study (49,200 m^3 per day), and that individual and total amounts of aromatic hydrocarbons discharged daily were quite similar.

During the winter months the rate of ballast processing increases significantly, reflecting heavy seas and the need for more ballast in the holds of vessels for the safe passage of the tanker fleet. The quantities of aromatic hydrocarbons discharged daily during the winter months increases correspondingly.

Based on the experimental data reported here, it appears that during the studied summer months of plant operation, 221 to 265 L of aromatic hydrocarbons were discharged daily into Port Valdez. Benzene contributed approximately 114 L per day, toluene 102 L per day, and xylenes 45 L per day to this volume. During the winter months (February 19 - March 2, 1979) of plant operation, approximately 462 L of aromatic hydrocarbons were discharged daily from the treatment plant into receiving waters. Benzene was discharged at an average rate of 191 L per day, while the toluene discharge rate was 181 L per day, and xylenes were discharged at a rate of 90 L per day.

The relationship between volume of water processed and the absolute quantities of aromatic hydrocarbons discharged into Port Valdez was established from the data collected during the Summer 1978 study and Winter and Summer

TABLE 19. ESTIMATED DAILY DISCHARGE OF ORGANIC MATTER, FIRST SUMMER STUDY, AUGUST 1978

	Date, 1978											
	8/7	8/8	8/9	8/10	8/11	8/12	8/13	8/14	8/15	8/16	Total	Daily Average
	Volume of Water Discharged (in thousands of cubic meters/day)											
	34	15	38	30	72	79	61	42	23	64	458	45
	Organic Compounds Discharged (liters/day)											
Benzene	106	23	57	76	144	254	235	140	42	163	1238	124
Toluene	72	23	53	64	114	220	140	117	42	140	984	98
Xylenes/ Ethylbenzene	23	15	30	34	64	121	83	57	19	64	511	51
Total Aromatic Hydrocarbons	201	61	140	174	322	595	458	314	102	367	2733	273
Dissolved Nonvolatile Organics	147	53	159	129	318	254	273	159	61	182	1733	173
Suspended Organics	114	15	91	91	0	280	102	83	38	26	840	84

TABLE 20. ESTIMATED DAILY DISCHARGE OF ORGANIC MATTER, WINTER STUDY, FEBRUARY 1979

	Date, 1979											
	2/19	2/20	2/21	2/22	2/23	2/24	2/26	2/28	3/1	3/2	Total	Daily Average
	Volume of Water Discharged (in thousands of cubic meters/day)											
	98	98	95	98	95	95	45	95	95	95	908	91
	Organic Compounds Discharged (liters/day)											
Benzene	314	148	208	295	201	227	61	182	144	132	1911	191
Toluene	257	159	201	254	189	227	53	170	159	144	1813	181
Xylenes/ Ethylbenzene	117	98	106	98	83	95	27	95	83	95	897	90
Total Aromatic Hydrocarbons	689	405	515	647	473	549	140	447	386	371	4621	462
Dissolved Nonvolatile Organics	572	462	541	492	511	511	208	428	447	541	4712	471
Suspended Organics	314	-	-	79	284	38	15	-	125	-	855	86

TABLE 21. ESTIMATED DAILY DISCHARGE OF ORGANIC MATTER, SECOND SUMMER STUDY, JUNE 1979

	Date, 1979												
	6/19	6/20	6/21	6/22	6/24	6/25	6/26	6/27	6/28	6/29	6/30	Total	Daily Average
	Volume of Water Discharged (in thousands of cubic meters/day)												
	45	61	34	34	57	23	87	91	57	34	34	556	49
	Organic Compounds Discharged (liters/day)												
Benzene	68	159	95	53	170	8	155	208	121	72	57	1166	106
Toluene	87	151	87	45	148	11	155	208	114	64	53	1124	102
Xylenes/ Ethylbenzene	45	49	30	15	57	15	68	98	45	26	23	473	43
Total Aromatic Hydrocarbons	201	360	212	113	375	34	379	515	280	163	132	2763	251
Dissolved Nonvolatile Organics	110	-	-	189	303	83	341	344	182	102	-	1654*	208
Suspended Organics	72	-	-	136	178	26	42	117	98	42	-	712*	91

* Total for 8 days.

TABLE 22. AVERAGE DAILY DISCHARGE (IN LITERS) OF VOLATILE HYDROCARBONS DURING SUMMER 1978, WINTER 1979, AND SUMMER 1979 STUDIES

	Summer 1978	Winter 1979	Summer 1979
Average Daily Discharge of Ballast Water (thousands of cubic meters) m^3	45	91	49
Benzene (liters)	124	191	106
Toluene (liters)	98	181	102
Xylenes (liters)	51	90	43
TOTAL	273	462	250

1979 studies. Plotted in Figure 3 are daily volumes of water processed versus volume of aromatic hydrocarbon discharged. From this plot it can be calculated that with discharge of each 1 million gallons (3785 m^3) of treated ballast water, 22 L of aromatic hydrocarbons (benzene, toluene, and xylenes/ethylbenzene) are discharged.

Using this figure and volume of water processed, it is possible to calculate an approximate daily, monthly, and yearly discharge of aromatic hydrocarbons into Valdez Harbor. Such calculations were performed for each month of the first 2 years of plant operation by plugging daily flowrate into the equations for the curve in Figure 3 to get the daily volume of aromatic hydrocarbons and summing to obtain monthly totals. The results are reported in Table 23. In addition to volume of aromatic hydrocarbon discharged monthly, the corresponding figures for volume of ballast processed and the amount of oil and grease (as determined by the gravimetric procedure) are also reported in the same table.

As can be seen from the reported data, during the first 5 months of plant operation in 1977 approximately 5322 L of aromatic hydrocarbons were discharged monthly, for a total of approximately 26,500 L. In 1978 the monthly rate of aromatic hydrocarbons discharged rose to approximately 8501 L for a 12-month total of approximately 102,200 L. The rate of monthly discharge of aromatic hydrocarbons during the first 7 months of 1979 was approximately 9296 L.

All in all, during the first 2 years of treatment plant operation, approxiamtely 193,000 L of aromatic hydrocarbons were discharged into Port Valdez.

Quality of Final Effluent

The quality and the maximum volume of final effluent discharged from the pipeline terminal facility into Port Valdez is stipulated in operating permits

1 gal = 3.785 l

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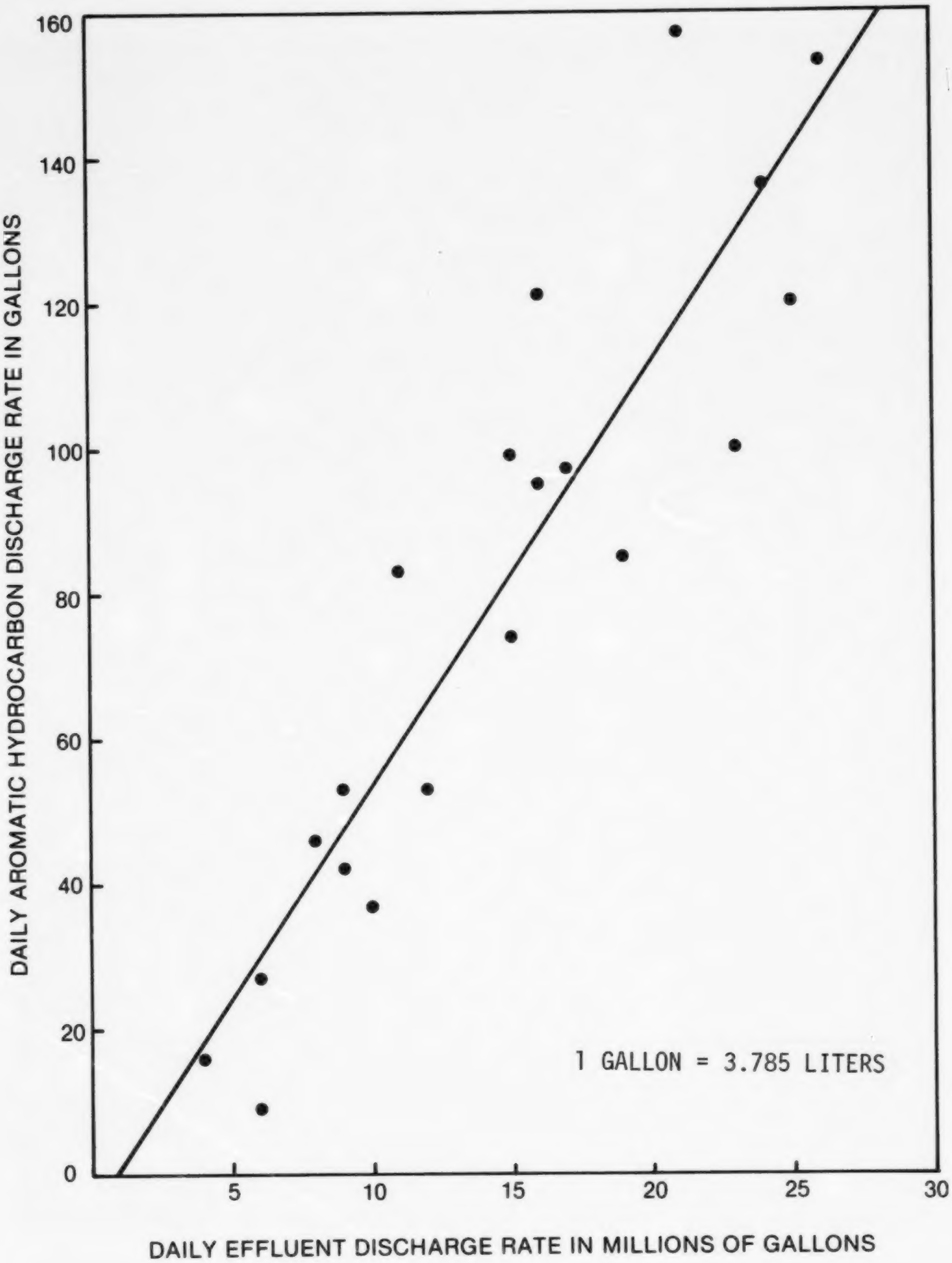

Figure 3. Volumes of aromatic hydrocarbons as a function of plant discharge rate.

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TABLE 23. DISCHARGE VOLUMES DURING FIRST 2 YEARS OF TREATMENT PLANT OPERATIONS

Date	Volume of Effluent Processed (thousands of cubic meters)	Volume of Oil and Grease Discharged (liters)*	Volume of Aromatic Hydrocarbons Discharged (liters)**
August 1977	590.1	1,298	3,422
September 1977	905.8	2,263	5,254
October 1977	886.4	1,597	5,140
November 1977	1,109.0	5,212	6,431
December 1977	1,097.7	5,378	6,366
1977 Monthly Avg	917.9	3,149	5,322
January 1978	1,089.7	4,686	6,321
February 1978	1,272.9	5,855	7,385
March 1978	1,191.1	4,406	6,908
April 1978	1,644.6	5,098	9,538
May 1978	1,533.7	6,593	8,895
June 1978	1,588.2	10,163	9,213
July 1978	1,610.5	7,445	9,341
August 1978	1,568.9	9,258	9,099
September 1978	1,334.6	7,339	7,740
October 1978	1,455.7	7,570	8,467
November 1978	1,544.3	8,032	8,955
December 1978	1,756.2	9,485	10,185
1978 Monthly Avg	1,465.9	7,036	8,501
January 1979	1,691.5	8,119	9,811
February 1979	1,752.1	10,689	10,163
March 1979	1,940.6	7,956	11,257
April 1979	1,535.2	5,375	8,902
May 1979	1,676.8	6,037	9,724
June 1979	1,041.3	2,914	6,041
July 1979	1,582.9	3,482	9,182
1979 Monthly Avg	1,602.9	6,253	9,296
Total amount discharged over 2 years of plant operation	33,398.8	143,955	193,743

* From plant records as reported by Alyeska to the State of Alaska DEC.

** Calculated from experimental data and plant records as reported to State of Alaska DEC.

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issued by the U.S. Environmental Protection Agency and the Alaska Department of Environmental Conservation to the Alyeska Pipeline Service Company. The permit (expiration date, December 1, 1979) specifies volumes of permissible daily discharge of the treated effluent, levels of oil and grease in the effluent, and limits for pH. Periodic measurements are also made for suspended solids, BOD, and phenol. Oil and grease values were the principal water quality parameters monitored daily during the first 2 years of plant operation. This value was determined by the extraction-gravimetric procedure using 24-hour composite samples.

The operating permit specified daily average for oil and grease at 8 mg/L and daily maximums at 10 mg/L. Examination of records (summarized in Table 24) for the first 2 years of plant operation reveals that the treatment plant produced effluent consistently within the limits specified in the permit. During the first 5 months of plant operation (August-December 1977), the average daily level for oil and grease was 3.2 mg/L, a value well below permit specifications of 8 mg/L. The monthly average volume of water processed during this period was approximately 918,000 m^3. The plant operation intensified in 1978 and 1979 and the volume of ballast processed rose to approximately 1,514,000 m^3 per month. The level of oil and grease in the final effluent rose correspondingly to approximately 4.2 mg/L, still well below permit specifications.

The oil and grease values, however, do not reflect completely the chemical composition of the final effluent. We have found that the treated effluent contains, in addition to suspended organic matter of petroleum origin, substantial amounts of volatile and nonvolatile dissolved organic compounds. As a matter of fact, it was found that suspended petroleum fraction was the smallest, and probably the least significant, chemical component of the discharged effluent. It contributed on the average only 10% to 20% to the total organic load of the final effluent. The largest single group of organic compounds present in the final effluent were aromatic hydrocarbons. Volatile aromatic hydrocarbons alone (benzene, toluene, and xylenes/ethylbenzene) accounted for almost half of the organic matter discharged from the plant into Port Valdez waters. In addition to volatile aromatic hydrocarbons, nonvolatile aromatic compounds (phenolics and naphthalenes) were found in the discharged water. The dissolved nonvolatile fraction (35% to 40% of the total organic load) contained phenolic compounds in concentrations of 0.5 to 0.6 ppm and naphthalene and alkyl naphthalenes in concentrations of 0.2 to 0.3 ppm. Those compounds are considered by many to be toxicologically significant.

The result of this study proved that total material balance of organic matter in the final effluent is the best measure of the water quality. As far as the oily wastewaters are concenred, such balance can be defined as the sum of suspended and dissolved organic matter. Dissolved organic matter can be further subdivided into volatile and nonvolatile fractions.

In the case of treated effluent from the large-scale ballast treatment operation, a definition of organic material balance can be derived from concentrations of volatile hydrocarbons, dissolved nonvolatile organics, and suspended organic matter. The average values for these three parameters of water quality as measured during the Summer 1978, Winter 1979, and Summer 1979 studies are presented in Table 16.

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TABLE 24. MONTHLY VOLUMES OF BALLAST PROCESSED AND AVERAGE CONCENTRATIONS OF OIL AND GREASE (BY GRAVIMETRIC METHOD)*

Date	Volume of Effluent Processed (thousands of cubic meters)	Monthly Average Oil and Grease (mg/L)
August 1977	590.1	2.2
September 1977	905.8	2.5
October 1977	886.4	1.8
November 1977	1,109.0	4.7
December 1977	1,097.7	4.9
1977 Average	917.9	3.2
January 1978	1,089.7	4.3
February 1978	1,272.9	4.6
March 1978	1,191.1	3.7
April 1978	1,644.6	3.1
May 1978	1,533.7	4.3
June 1978	1,588.2	6.4
July 1978	1,610.5	4.6
August 1978	1,568.9	5.9
September 1978	1,334.6	5.5
October 1978	1,455.7	5.2
November 1978	1,544.3	5.2
December 1978	1,756.2	5.4
1978 Average	1,465.9	4.8
January 1979	1,691.5	4.8
February 1979	1,752.1	6.1
March 1979	1,940.6	4.1
April 1979	1,535.2	3.5
May 1979	1,676.8	3.6
June 1979	1,041.3	2.8
July 1979	1,582.9	2.2
1979 Average	1,602.9	3.9
Overall Average	1,391.7	4.2

* From plant records as reported by Alyeska to State of Alaska DEC.

The relative importance of individual organic fraction present in the final effluent becomes quite apparent when one examines values of aromatic hydrocarbons, dissolved nonvolatile matter, and suspended matter discharged daily by the plant. This data is presented in Table 25. As can be seen from this table, approximately 329 L of aromatic hydrocarbons, 283 L of dissolved organic matter, and 87 L of suspended petroleum were discharged daily from the plant into the receiving waters of Port Valdez during the period of this study.

The data reported here indicates a need for redefining water quality standards for treated oily wastewater discharges. A first step in that direction was taken by the State of Alaska in February 1979. A limit on aromatic hydrocarbon concentration was specified in the State Water Quality Standards (4). Additionally, the State undertook an 18-month study on the ecological significance of discharged aromatic hydrocarbons and the results of this study could form a foundation for specific regulations regarding discharges from oil processing and handling facilities.

Comparison of Analytical Methods

The current principal method for "total oil" determination is based on extraction into nonpolar solvent (Freon 113 is commonly used), followed by IR or gravimetric quantification. The IR procedure requires calibration either by arbitrarily designated mixtures of hydrocarbons, or by a standard solution made from the type of oil being analyzed. For this method to be effective and accurate, the chemical composition of both standard and test materials must be constant and similar to each other. The gravimetric procedure involves evaporation of the solvent and weighing of the residue. Lower molecular weight hydrocarbons are usually lost during the evaporation step, and this procedure quite often yields lower results than the IR method.

The principal limitations of the standard methods include incompleteness of mass transfer from aqueous into nonaqueous phase during liquid-liquid

TABLE 25. AVERAGE DAILY DISCHARGE OF ORGANIC MATTER FROM THE TERMINAL TREATMENT FACILITY

	Liters per Day			
	Summer 1978 Study	Winter 1979 Study	Summer 1979 Study	Average
Volatile Aromatic Hydrocarbons	273	462	250	329
Dissolved Nonvolatile Organic Matter	174	473	208	283
Suspended Organic Matter	83	87	91	87

extraction, loss of volatile fraction during solvent evaporation in the gravimetric procedure, and different absorption characteristics of aromatic and aliphatic hydrocarbons in the IR region.

One of the objectives of this study was to determine the relationship between total organic content of oily wastewaters (organic material balance) and solvent extraction methods followed by either infrared spectrometric or gravimetric procedures. To do so, standard methods for oil analysis (8) 502A and 502B were used daily for characterization of oil content of the process stream during the first field study in Summer 1978.

Tables 26 and 27 report data on the relationship between TOL and "total oil" determination by Freon 113 extraction and IR and gravimetric determination. Examination of this data reveals that the Freon 113 extraction - IR method (Standard Method 502B) recovers on an average 36% of the total organics

TABLE 26. RELATIONSHIP BETWEEN TOTAL ORGANIC LOAD AND EXTRACTION-IR AND EXTRACTION-GRAVIMETRIC METHODS FOR TOTAL OIL

August '78 (day):	7	8	9	10	11	12	13	14	15	16	Avg
Final Effluent:											
Total Organic Load, mgC/L	13.0	7.7	10.0	12.4	8.5	13.4	13.1	12.7	8.4	8.4	10.7
Total Oil, Extraction-IR Method, mg/L	5.5	1.6	2.2	3.5	1.0	10.7*	3.9	7.7	1.9	1.1	3.9
Extraction-Gravimetric Method, mg/L	3.6	1.6	1.3	2.0	1.9	7.9*	3.1	4.7	2.3	1.1	3.0

Gravity Separator Effluent:			
August '78 (day):	17	18	Avg
Total Organic Load, mgC/L	16.2	23.3	19.8
Total Oil Extraction-IR Method, mg/L	16.4	15.1	16.0
Total Oil Extraction-Gravimetric Method, mg/L	7.2	8.9	8.0

* Hydrogen sulfide was present in the sample.

TABLE 27. RELATIONSHIP BETWEEN TOTAL ORGANIC LOAD* AND TOTAL OIL DETERMINATION**

	Gravity Separator	Final Effluent	Approximate % Recovery Gravity Separator	Approximate % Recovery Final Effluent
Total Organic Load, mgC/L	20	11		
Total Oil, Method 502B, mg/L	16	4	80	36
Total Oil, Method 502A, mg/L	8	3	40	27

* Total organic load = sum of all volatile and nonvolatile organics.

** Total oil determination: Method 502A - Freon extraction-gravimetric
Method 502B - Freon extraction-IR detector

present in the final effluent. The recovery values for the effluent from the gravity separator, however, were higher -- close to 80%.

The fluctuations in percent recovery of organic matter by the Freon 113-Extraction IR method were quite wide in samples of final effluent. The range was from a low of 13% to a high of 80%. The accuracy of this measurement appears to depend on the composition of organic matter in the final effluent; the lowest recovery value was observed on a day (August 16) when the level of aromatic hydrocarbon was the highest (62% of TOL). The low contribution of aromatic hydrocarbons to IR absorptance at 2927 cm^{-1} was the probable cause of this very low recovery. The highest recovery value (80% of TOL) was observed on a day (August 12) that the tanker Brooks Range arrived from Panamanian waters. The ballast waters from tankers departing from Panama are known to contain significant concentrations of hydrogen sulfide and other sulfur-containing compounds that were most likely generated as a result of biodegradation of crude during the passage. The treated effluent samples collected on August 12 did indeed smell strongly of hydrogen sulfide and were yellow in color. It is hypothesized that the presence of sulfur compounds on that day might have contributed significantly to the relatively high value of "total oil" recovery.

The "total oil" analysis by the gravimetric procedure (Standard Method 502B) produced the lowest recovery of TOL on a day (August 16) when aromatic hydrocarbon content of the sample was the highest (62%). The explanation for this is rather obvious: principal organic components of the effluent (benzene, toluene, and xylenes) were lost during sample evaporation prior to weighing of the residue. The highest recovery of TOL by the gravimetric method of measuring "total oil" occurred on August 12 during the processing of hydrogen-sulfide-containing ballast originating in Panamanian waters. The presence of sulfur-containing compounds could also contribute to this relatively high order of recovery.

Standard methods for analysis of oil and grease are important means in determining free oil content of oily wastewaters. They are less effective, however, in analyzing samples containing large proportions of aromatic hydrocarbons since aromatic hydrocarbon response at 2927 cm^{-1} is much lower than that of aliphatic hydrocarbons. The combined use of IR and UV for analysis of oily wastewater extracts might overcome this difficulty. While aromatic hydrocarbons respond poorly in the IR region, they respond rather well in the UV region of the spectrum. The inverse is true of aliphatic hydrocarbons. Calibration and analysis of aliphatic hydrocarbons by IR and aromatic hydrocarbons by UV might overcome observed difficulties of analysis while providing more information on the chemical composition of the sample.

As a result of these studies it was concluded that an additional study on the distribution of the aromatics in the receiving waters appeared necessary. This study is reported in Section 5.

SECTION 5

FJORD STUDY

INTRODUCTION

Current pollution control practices require that the receiving waters be protected from harmful effects of compounds that might be present in effluents from industrial operations and municipal waste discharges. The enforcement of such practices is carried out largely by the Environmental Protection Agency and state agencies under the National Pollutant Discharge Elimination System (NPDES) permit program. Discharge permits usually specify effluent limitations and monitoring requirements. Such limitations are, ideally, designed in such a way that no chemical composition will enter receiving waters in concentrations harmful to biota. LD_{50} values of a given chemical material relative to selected species native to the receiving environment can be used as a guide in arriving at the discharge limitations. In practice, however, it is extremely difficult to reduce concentrations of many chemical compositions present in treated effluent to a point at which they do not exhibit some degree of toxicity to biota.

To overcome this difficulty, a practice of establishing mixing zones, in which chemicals can be present in concentrations harmful to biota, is becoming common. In this practice, water quality standards and requirements are suspended or lowered for a specified volume of receiving water, usually in the immediate vicinity of the discharge outfall. The prevailing water quality standards, however, must be maintained outside the mixing zone, so as to protect the health and well-being of the overall ecosystem in the affected water body. Such practices address in a realistic way the "real-life" problems of pollutant discharge controls.

The "mixing zone" approach to pollution control has become codified in some states, including Alaska (Water Quality Standards, State of Alaska, Provision 18AAC70.032, Register 69, April 1979, Alaska Department of Environmental Conservation [ADEC], Juneau, Alaska). The provisions for Alaska's water quality standards state that:

> "The department (ADEC) will in its discretion prescribe in wastewater discharge permits a volume of dilution for the effluent within the receiving waters. Water quality standards may be exceeded within this mixing zone; however, the standard shall be met at every point outside its boundaries."

The dimensions of mixing zones are usually defined by its boundaries: horizontal (top, bottom) and vertical (sides and ends). Such boundaries enclose a specific volume of water and the required dilution factors can be calculated from volume of discharge, concentration of pollutant in the effluent, and permissible levels of concentrations outside the mixing zones.

An example of mixing zone specifications can be found in the operating permit (expiration date, December 1, 1979) issued to the Alyeska Pipeline Service Company, which operate the marine terminal ballast water treatment plant in Valdez, Alaska:

1. The top of the mixing zone shall be at all times 5 meters below the receiving water surface.

2. The bottom of the mixing zone shall be at all times 1/2 meter above the bottom of Port Valdez.

3. The sides of the mixing zone shall be not more than 150 meters from the diffuser centerline.

4. The ends of the mixing zone shall be not more than 150 meters from each end of the 63-meter diffuser.*

The position of the mixing zone is shown in Figure 4. In essence, it is a prism 300 meters long and 150 meters deep at the outer boundary, extending 360 meters from the shoreline. A volume of the zone can be calculated from these dimensions as 8.1 million cubic meters. The daily average discharge flow from the treatment plant is specified in the permit as 102,000 cubic meters. From this it can be calculated that the ratio of the daily discharge volume to the volume of the mixing zone is approximately 1:80. In ideal situations, the discharging effluent should uniformly and evenly mix with the receiving water within the confines of this specified prism to provide for maximum dilution within the limits of the mixing zone. Utilization of the total volume of the mixing zone would assure that the chemical composition present in the discharge is sufficiently diluted so as not to exceed the water quality standards at the boundaries of the zone.

In order to determine the effectiveness of the mixing zone approach in diluting effluent from point source discharges, an experimental program was carried out in Port Valdez near the outfall of the Alyeska treatment plant. Dispersion and persistence of the effluent was monitored by determining concentration gradient of aromatic hydrocarbons that are discharged from the plant.

PORT VALDEZ

The physical oceanography of Port Valdez is well defined by studies of Hood (1), Colonell (2) and coworkers. They report that Port Valdez is about 5 km wide by 18 km long and is shaped somewhat like a bathtub, with steep sides on the north and south and a nearly horizontal bottom at a depth of about 240 meters over three-quarters of its length. In the easternmost quarter of the

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* The diffuser is 63 meters in length and the effluent is discharged along the entire length.

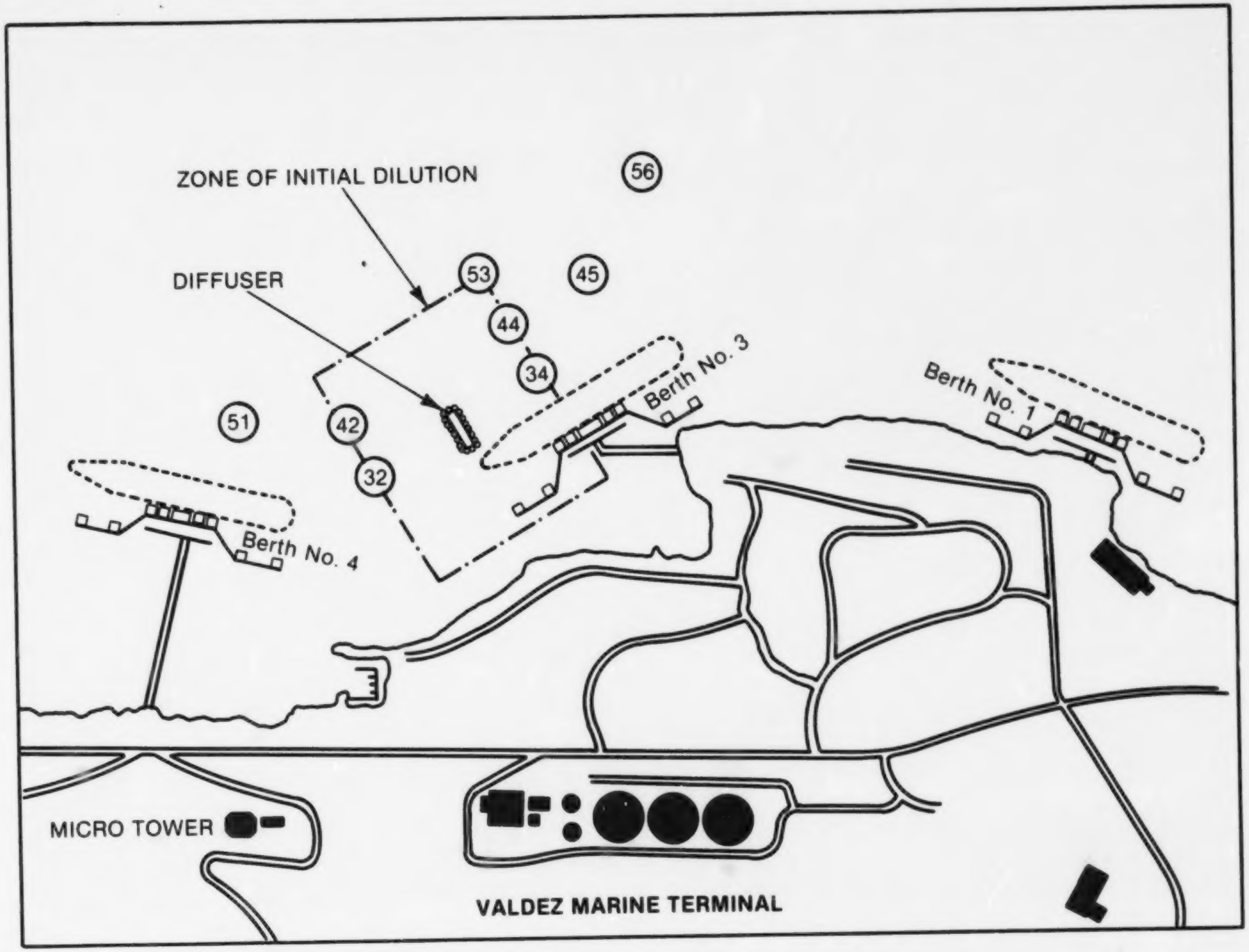
ZONE OF INITIAL DILUTION
DIFFUSER
56
53
45
44
34
51
42
32
Berth No. 3
Berth No. 1
Berth No. 4
MICRO TOWER
VALDEZ MARINE TERMINAL

Figure 4. Location of outfall diffuser and mixing zone.*

* Numbers refer to sampling stations.

fjord the bottom rises rather uniformly to the eastern shore at the former townsite of Valdez. The maximum depth of Port Valdez is 247 meters (in the southwestern corner), while the overall mean depth of the fjord is about 180 meters. The fjord of Port Valdez extends about 23 km eastward from Valdez Narrows, a narrow silled entrance that is regarded as the demarcation between Port Valdez and Valdez Arm. The town of Valdez lies near the northeast corner of the fjord, while the Alyeska Marine Terminal is on the south shore at Jackson Point. The waters of Port Valdez and Valdez Arm exhibit a pronounced annual cycle of variation between strongly stratified summer and early autumn conditions to a nearly homogeneous state that persists from late fall through winter to early spring. Examples of thermal and density stratification during different seasonal cycles are shown in Figures 5 and 6.

Until August 1977, the waters of Port Valdez had been essentially in a pristine and unpolluted condition, as reported in baseline studies conducted by Hood and coworkers (9) in the early Seventies. In August 1977 the flow of oil began through the TransAlaskan pipeline, and the ballast treatment plant at the terminal facility became operational. The oil tankers began to arrive from southern ports partially loaded with ballast water. This is required in order to provide open sea stability for empty tankers as they sail north along the Pacific shores of the North American continent. The water is contained in compartments previously occupied by oil, and thus becomes contaminated by the oil. The oil concentration in the untreated ballast water averages approximately 0.7%, or 7000 ppm. Consequently, the ballast water must be treated before it can be safely discharged into Valdez Harbor.

The ballast treatment plant, as is described in Section 4, performs such a function by reducing the oil concentration (from 7000 ppm to below 8 ppm) using gravity separation and aeration-flotation methods of treatment (6). During the first year of plant operation, the average daily discharge rate was 39,743 m^3. This figure rose to approximately 52,990 m^3 per day in the second year. Approximately 34 million m^3 of treated ballast were discharged into the receiving waters of Port Valdez between August 1977 and August 1979 (Table 28).

The quality of the discharged effluent was monitored during the initial 2 years of plant operation by gravimetric determination of the oil. Additionally, Rockwell International carried out a study on the effectiveness of treatment plant operations in the 1978-1979 time period. As part of this study, the chemical composition of the treated effluent was characterized in gross and detailed chemical terms. The study has shown that organic matter in ballast waters (treated and untreated) was composed of three principal fractions: dissolved volatile hydrocarbons, dissolved nonvolatile organics, and suspended nonvolatile organic matter. The average chemical composition of organic compounds in the effluent appeared to be quite constant and was not affected by the seasonal variations. As a matter of fact, remarkable similarity in the composition was observed during the three experimental time sequences, as shown in Table 23. Aromatic hydrocarbons, composed largely of benzene, toluene, and xylenes/ethylbenzene, comprised by far the largest portion of organics in the treated wastewater.

Based on plant operating records and extrapolating from the average chemical composition of the treated effluent, it can be calculated that during the

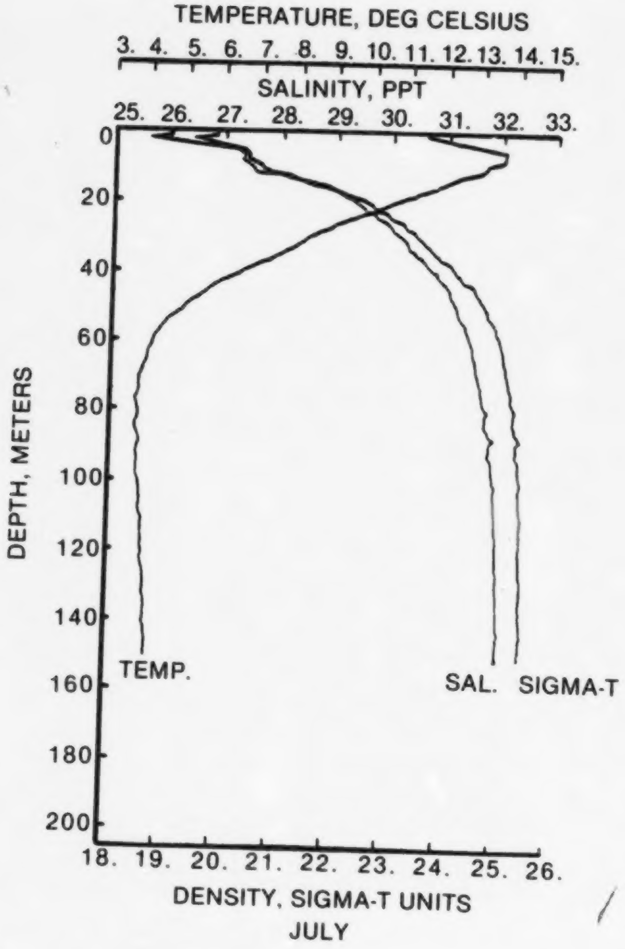

Figure 5. Temperature, salinity, and density stratification in Port Valdez, summer conditions.*

Sigma-T = $(\rho-1) \cdot 10^3$, where ρ = density in gm $\cdot$ cm^{-3}

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* According to Colonell (2).

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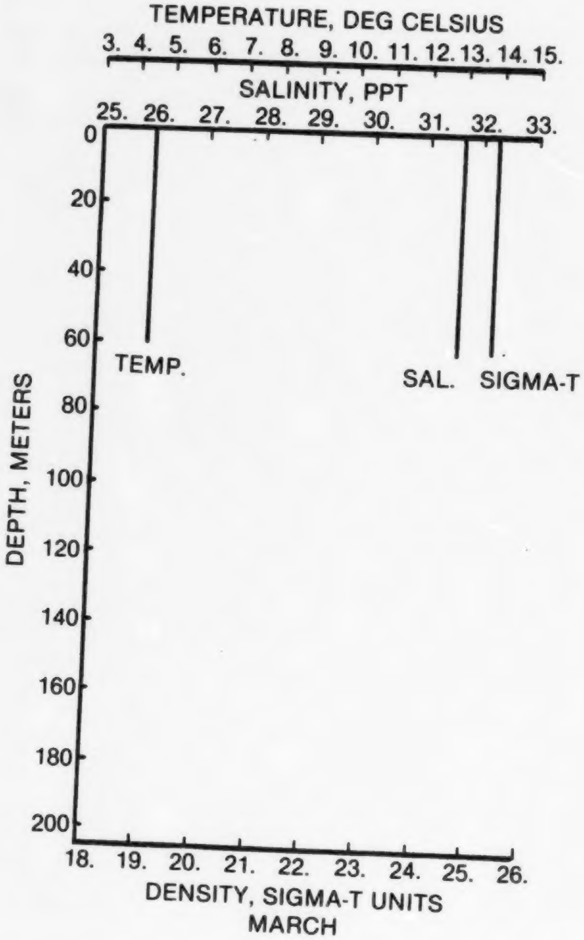

Figure 6. Temperature, salinity, and density stratification in Port Valdez, winter conditions.*

Sigma-T = $(\rho-1) \cdot 10^3$, where ρ = density in gm $\cdot$ cm^{-3}

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* According to Colonell (2).

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TABLE 28. MONTHLY RECORD OF DISCHARGES OF TREATED BALLAST WATER, FIRST AND SECOND YEARS OF PLANT OPERATION, TERMINAL FACILITY, VALDEZ, ALASKA*

First Year	Volume (thousands of cubic meters)	Second Year	Volume (thousands of cubic meters)
August 1977	590.1	August 1978	1,568.9
September 1977	905.8	September 1978	1,334.6
October 1977	886.4	October 1978	1,455.7
November 1977	1,109.0	November 1978	1,544.3
December 1977	1,097.9	December 1978	1,756.2
January 1978	1,089.7	January 1979	1,691.5
February 1978	1,272.9	February 1979	1,752.1
March 1978	1,191.1	March 1979	1,940.6
April 1978	1,644.6	April 1979	1,535.2
May 1978	1,533.7	May 1979	1,676.8
June 1978	1,588.2	June 1979	1,641.3
July 1978	1,610.5	July 1979	1,582.9
TOTAL	14,565.0	TOTAL	18,933.0
Monthly Average	1,215.0	Monthly Average	1,578.0
Daily Average	39.7	Daily Average	51.9

* From plant records as reported to State of Alaska DEC.

first year of plant operation, 208 L of dissolved aromatic hydrocarbons were discharged daily. This volume rose to 269 L per day during the second year of plant operation. It can be estimated that during the 2 years of plant operation, approximately 193,000 L of aromatic hydrocarbons were discharged into the rather sheltered waters of Port Valdez (Table 23).

The reported data indicate a slightly rising input of well-defined chemical composition into receiving waters that were essentially pristine prior to August 1977. Studies carried out by the Institute of Marine Science of the University of Alaska and Auke Bay Marine Fisheries Laboratory (NOAA) (10) on the fate and effect of this discharge have not yet disclosed either diffusion

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and dispersion paths for aromatic hydrocarbons, or long-term effects on the receiving environment. At this time, two critical points related to the ecology of Port Valdez remain unanswered:

1. Diffusion and dispersion paths of discharged pollutants under stratified and unstratified conditions in the receiving water
2. Long-term effect on chemical-biological steady state in the harbor

EXPERIMENTAL

The study of dissipation processes can best be carried out by monitoring the decay of the concentration of specific chemical compounds originally present in the effluent. Such concentration decays reflect the total sum of all environmentally significant processes, and are the true indication of pollutant dissipation in the receiving environment.

It was our intent to study the sum of all dissipation processes by monitoring the concentration of chemical compounds present in the discharging effluent. As indicated previously, benzene, toluene, and xylenes/ethylbenzene constitute approximately 50% of the total organic load in the discharge, and are significant due to their toxicological effects (11). For those reasons, we selected aromatic hydrocarbons as an indication of the overall process of pollutant dissipation in the receiving environment.

An analytical methodology capable of accurate measurement of total volatile aromatic hydrocarbon at 0.5 parts per billion (ppb) levels was developed and used in this study. The details of this methodology are described in Appendices G and H.

During the summer of 1979 two separate studies were carried out in Port Valdez -- one in June-July and one in September.

June-July 1979 Study

The scope of the June-July 1979 study included test and evaluation of various chemical and oceanographic techniques and procedures required for implementation of a full-scale harbor study. The specific objectives included:

1. Evaluation of the suitability of a Rider-type research vessel for the conduct of such studies
2. Selection of sampling stations in the harbor
3. Establishment and verification of navigational methods needed for location of sampling stations
4. Checkout of the suitability of oceanographic sampling equipment for multiple sampling (vertical) at selected sampling stations
5. Test of the sensitivity of analytical procedures for detecting low-ppb concentrations of aromatic hydrocarbons

The National Marine Fisheries Service (NOAA) research vessel stationed in Valdez was found to be a suitable platform for the conduct of the study. It was easily maneuverable and, in the hands of competent operating personnel, remained on accurately defined sampling stations for the required time periods during collection of multiple samples. During the sampling operations in the security zone, no scheduling problems or other conflicts with normal operation of the Alyeska Marine Terminal were experienced.

The observation grid developed by Colonell (2) for dispersion studies of the outfall diffusers was used as a guide in the selection of sampling stations (Figure 4). His dye diffusion studies indicated that the plume of discharge is formed in the vicinity of Berths 3 and 4 (see Figure 7), and is largely contained in a trap zone at a depth of 50 to 60 meters. During the summer months the contaminated zone assumed a horseshoe configuration facing offshore in a northerly direction (Figure 7).

Based on Colonell's predictive model (2), sample site numbers 42 and 51 were selected, and sampling was carried out at 40- and 60-meter depths at each station. This experimental design provided an indication of horizontal (from sample station 42 to sample station 51, a distance of approximately 175 meters), and vertical (from a depth of 60 meters to a depth of 40 meters, a distance of approximately 20 meters) dissipation of the concentration of aromatic hydrocarbons in the vicinity of the treatment plant outfall. An additional sample was taken at a depth of 60 meters at approximately a 2-km distance north from the terminal facility.

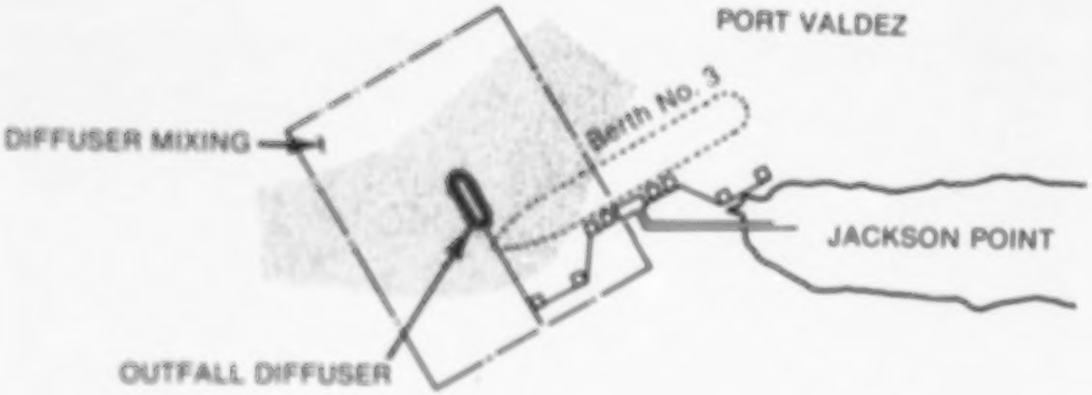
Detectable amounts of aromatic hydrocarbons were found at all sampling points, as shown in Table 29. Even the sampling point 2 km distant from the diffuser zone revealed the presence of aromatic hydrocarbons. Maximum concentrations of BTX (benzene, toluene, xylenes) were recorded at 60-meter depths at Station 42. The concentration of pollutants rapidly declined in the vertical plane (from 60 to 40 meters), and decayed much slower along the horizontal plane (from Station 42 to Station 51) (about 175 meters).

The results reported here appear to be in general conformity with the diffusion model postulated by Colonell, and indicate the existence of a trap zone at approximately 60-meter depths during summer conditions in Port Valdez.

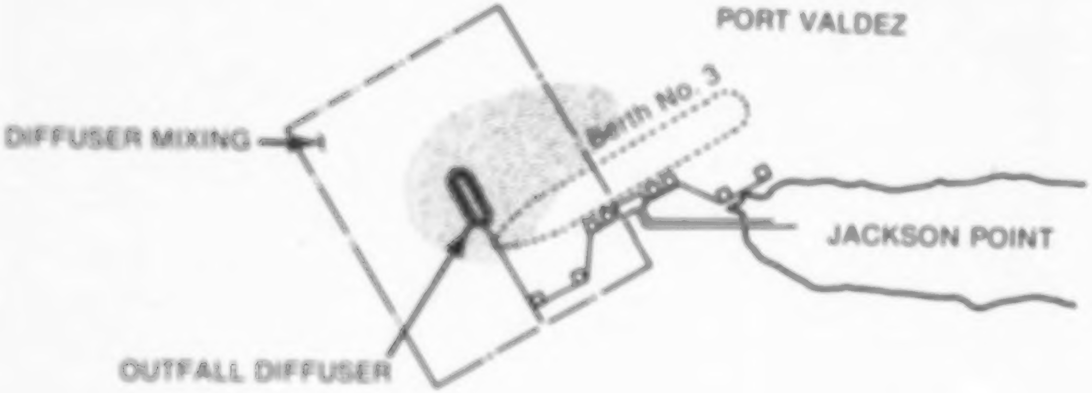
September 1979 Study

During the September study an attempt was made to detect and identify the position of the hydrocarbon-contaminated zone in the receiving waters of Valdez Harbor, and to determine the horizontal and vertical gradient (concentration decay) for aromatic hydrocarbons. To do so, a sampling scheme of vertical and horizontal transects was devised.

The vertical profiling of aromatic hydrocarbons was carried out at Station 42 (Figure 4) on the westerly boundary line of the mixing zone on September 14, 1979. Samples were taken at a depth of 77 meters (2 meters above the bottom), at 70, 60, 50, 40, 20, and 10 meters, and at the surface. Eight collected samples were analyzed for aromatic hydrocarbon content. The data is reported in Table 30. The sample with the highest concentration (21 micrograms/L [ppb]) was collected at a point 2 meters above the bottom (77-meter depth). The


PORT VALDEZ
Berth No. 3
DIFFUSER MIXING
JACKSON POINT
OUTFALL DIFFUSER

FIRST COLONELL DIFFUSER TEST (31 October—2 November 1977)


PORT VALDEZ
Berth No. 3
DIFFUSER MIXING
JACKSON POINT
OUTFALL DIFFUSER

SECOND COLONELL DIFFUSER TEST (19-21 April 1978)

Figure 7. Diffuser tests (approximate areal extent of observed minimum dilutions less than 80).*

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* According to Colonell (2).

TABLE 29. AROMATIC HYDROCARBONS IN VALDEZ HARBOR, JULY 1-6, 1979

Station No.	Bottom Depth, m	Sampling Depth, m	Total Aromatic Hydrocarbons, μg/L (ppb)	Benzene	Toluene	Xylenes/ Ethylbenzene
42	79	60	15.4	3.7	7.0	4.7
42	79	40	2.2	1.6	0.3	0.3
51	77	60	9.0	3.5	3.3	2.2
51	77	40	2.3	1.4	0.4	0.5
Midpoint (2 km north from discharge point)		60	2.8	2.0	0.4	0.4

TABLE 30. AROMATIC HYDROCARBONS IN VALDEZ HARBOR: VERTICAL DISTRIBUTION

Sampling Date: 14 September 1979

Sampling Site: Westerly boundary line of diffusion zone; Station 42 (Colonell)

Plant Discharge: 24 m^3 per minute, or approximately 34,560 m^3 per day

Depth, m	Total Aromatic Hydrocarbons, μg/L	Benzene, μg/L	Toluene, μg/L	Xylenes/ Ethylbenzene, μg/L	Temperature, °C
Surface	2.2*	0.6	0.8	0.8	10.5
10	< 0.5	-	-	-	13.2
20	< 0.5	-	-	-	12.9
40	0.7	0.1	0.3	0.3	10.9
50	0.7	0.2	0.3	0.2	9.3
60	0.9	0.1	0.4	0.4	8.0
70	2.4	0.6	0.9	0.9	7.0
77**	21.0	5.0	6.5	9.5	5.9

* Possible contributions from surface vessels.

** 2 meters off the bottom.

concentration rapidly decayed in the vertical plane. At a 70-meter depth (9 meters above the bottom) it dropped to 2.4 micrograms/L (ppb). This represents a concentration decay of about 3 ppb per 1 meter of depth. The concentration at 40-meter depth (39 meters above the bottom) was only 0.7 micrograms/L (ppb). The vertical profile of decay of aromatic hydrocarbon concentrations at Station 42 is shown in Figure 8.

Recorded data indicated that a trap zone for aromatic hydrocarbons (and probably other components of the discharged effluent) existed at near-bottom depths during hydrological conditions prevailing in September. Additional sampling was then carried out on September 18, 1979, on the boundary lines of the mixing zone and in the immediate vicinity. Samples were taken at Station 32 (westerly boundary of the mixing zone), Stations 34 and 44 (easterly boundary of the mixing zone), and Station 51 (adjacent to the westerly boundary line) (Figure 4). Samples were taken at 1 and 11 meters above the bottom.

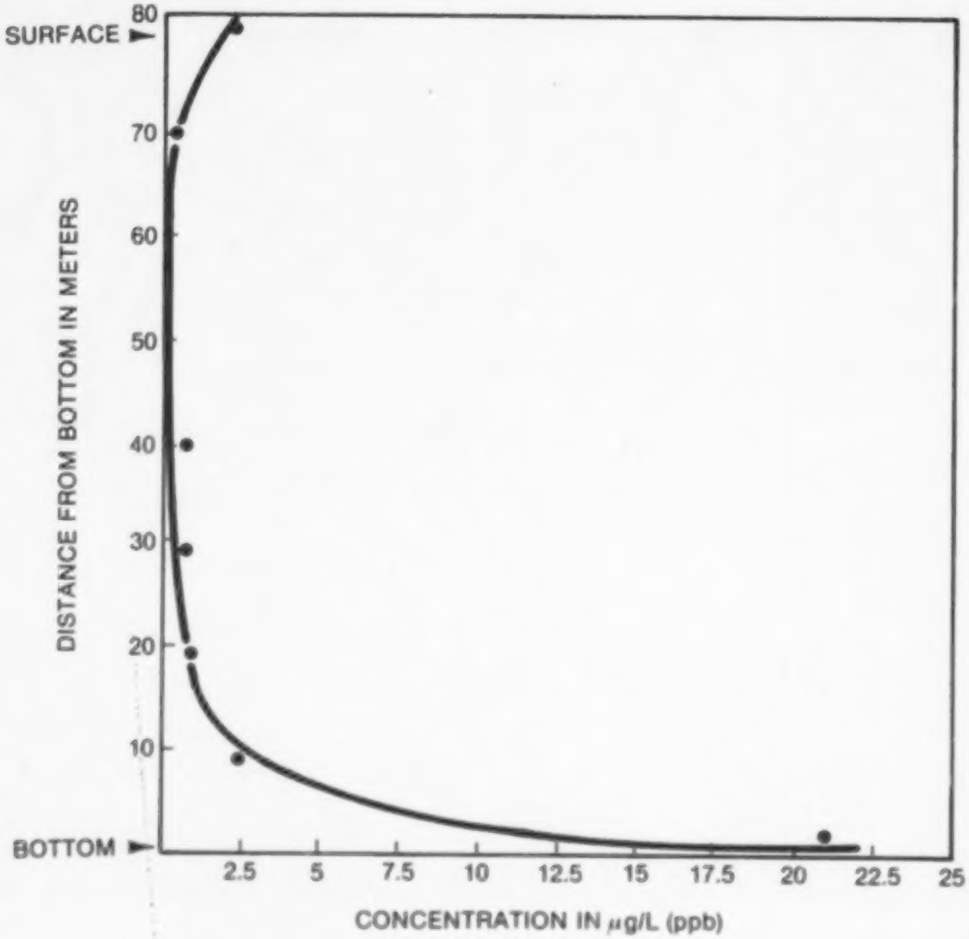

Figure 8. Concentration decay of aromatic hydrocarbons in vertical plane, Station 42, Port Valdez, Alaska, September 1979.

The results are reported in Table 31. The maximum concentration of aromatic hydrocarbons was found at a depth of 64 meters (88 micrograms/L [ppb]) at Station 32, and 66 meters (38 micrograms/L [ppb]) at Station 34.

The concentrations of aromatic hydrocarbons decayed rather rapidly in the vertical plane (both up and down). At Station 32, aromatic hydrocarbons decayed from 88 to 1.3 ppb within 10 meters on the vertical plane in the upper direction. This represents a drop in concentration of almost 9 ppb per 1 meter of depth. The concentrations also decayed on the vertical plane in the lower direction. Within a 10-meter depth, it dropped from 38 to 18 ppb at Station 34.

In the deep waters of Station 44 at a depth of 121 meters (1 meter above the bottom), only traces (0.5 micrograms/L [ppb]) of aromatic hydrocarbons were found. None were found at a depth of 75 meters.

The analysis of collected data suggests that a narrowly defined trap zone existed in Port Valdez in September 1979. The centerline of this zone was at depths of approximately 60 to 70 meters. The aromatic hydrocarbons were contained within this zone and their concentration rapidly decreased in the

TABLE 31. AROMATIC HYDROCARBONS IN VALDEZ HARBOR: NEAR-BOTTOM ENVIRONMENT

Sampling Date: September 18, 1979
Sampling Sites: Westerly and easterly boundaries of the diffusion zone
Plant Discharge: Approximately 18,925 m^3 per day

Station No.	Bottom Depth (m)	Sampling Depth (m)	Total Aromatic Hydrocarbons (μg/L)	Benzene (μg/L)	Toluene (μg/L)	Xylenes/Ethylbenzene (μg/L)	Temp., (°C)
32	65	54	1.3	0.4	0.4	0.5	7.5
32	65	64	88.0	39.0	18.0	31.0	6.8
34	77	66	38.0	18.0	8.0	12.0	6.1
34	77	76	18.0	8.0	6.0	4.0	5.6
44	122	75	< 0.5	-	-	-	5.6
44	122	121	0.5	-	-	-	5.0
51	77	76	< 0.5	-	-	-	5.5

vertical plane (up and down). This finding assumes greater importance if one examines thermal and density stratification of Port Valdez for this time of year.

As can be seen in Figure 5, both the thermocline and density stratification zone ends at a depth of 50 to 70 meters for the June-August time of the year. The upper stratified waters appear to function as a lid on the effluent, preventing its diffusion in the vertical plane.

To study the spread of aromatic hydrocarbons into the harbor, a horizontal transect of seven sampling stations was devised at uniform depths of 60 meters, which corresponded to approximately the depth at the beginning of the pronounced thermal and density stratification of the upper water column. The harbor sampling station locations are shown in Figure 9. Station B in Anderson Bay was designated as a reference site of pristine waters. No hydrocarbons were detected there and it was considered as a reference point in fjord studies.

On September 12-13, 1979, samples were collected at each sampling station at a depth of 60 meters, and then analyzed (see Table 32). Aromatic hydrocarbons were found at a 1.2-microgram/L (ppb) concentration at Station C, 3.5 km distant from the outfall in a northwesterly direction, and also at a 1.2-microgram/L (ppb) concentration at Station E, 2.5 km distant from the outfall in an easterly direction. No hydrocarbons were detected at other stations. From this data it appears that aromatic hydrocarbon horizontal spread can extend as far as 2 to 3 km from the discharge point into the harbor.

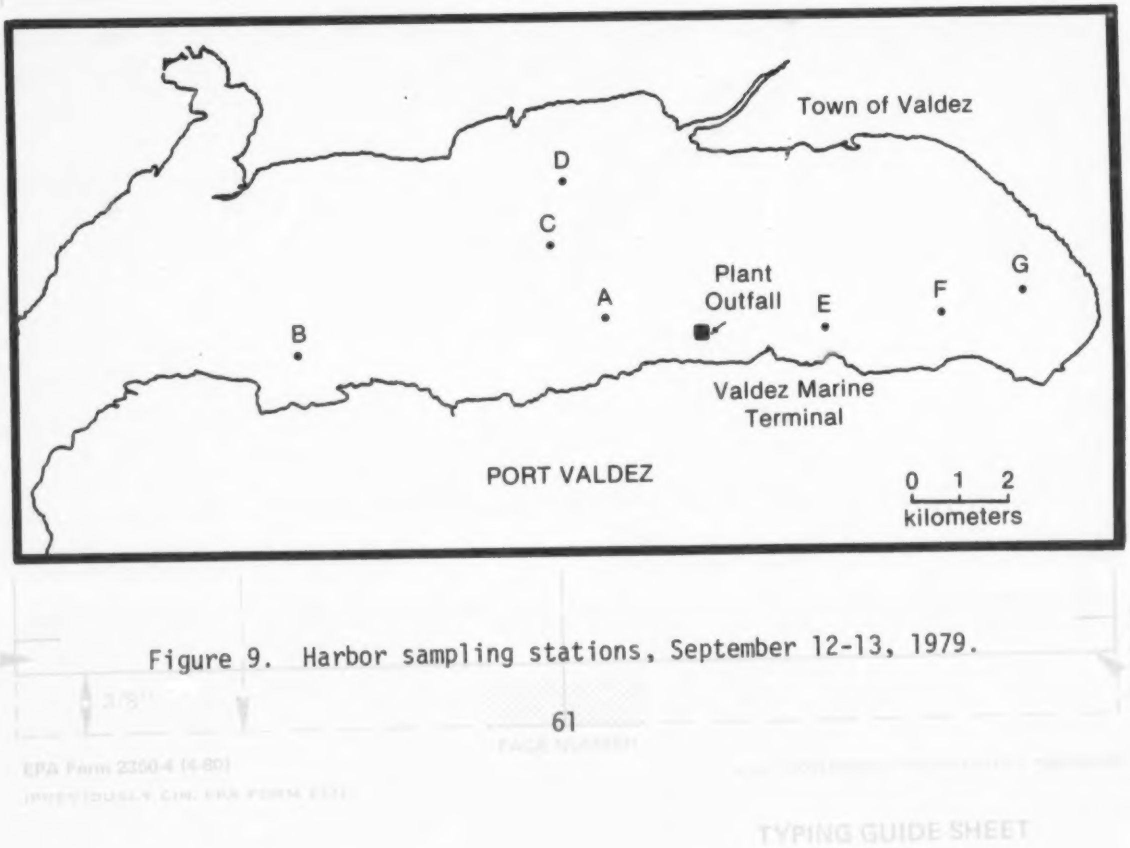

Figure 9. Harbor sampling stations, September 12-13, 1979.

TABLE 32. AROMATIC HYDROCARBONS IN VALDEZ HARBOR: HORIZONTAL DISTRIBUTION OUTSIDE THE DIFFUSER ZONE AT 60-METER DEPTHS

(Sampling Dates: September 12 and 13, 1979)

Station No.	Temperature (°C)	Total Aromatic Hydrocarbons (μg/L)	Benzene (μg/L)	Toluene (μg/L)	Xylenes (μg/L)
A*	5.5	< 0.5	-	-	-
B*	6.0	< 0.5	-	-	-
C*	5.5	1.2	0.7	0.3	0.2
D*	5.8	< 0.5	-	-	-
E*	6.0	1.2	0.3	0.2	0.7
F*	6.0	< 0.5	-	-	-
G*	-	< 0.5	-	-	-

* See map, Figure 9.

June 1980 Study

Additional diffusion studies were carried out in Port Valdez during June 3-13, 1980. Three stations were sampled on the boundary line of the mixing zone (42, 32, 34 [Figure 4]). Additionally, sampling was carried out at two stations near the mixing zone (45, 56) and at two control sites. Samples were collected at intervals of 10 meters on a vertical plane over 30- to 80-meter depths. Trace analyses were performed for benzene, toluene, xylenes, and ethylbenzene. Complementary physical measurements of water temperature, density, and salinity were also made.

The concentration decay of aromatic hydrocarbons in the vertical plane is illustrated by the data collected at Station 42, as shown in Table 33 and Figure 10. As can be seen from this data, the aromatic hydrocarbons are contained in a narrow (10 meters or less) concentrated trap zone at a depth of approximately 50 meters with very little indication of vertical diffusion either in the upper or lower reaches of the water table. The concentration decay (dilution) in the horizontal plane is illustrated by the data for sampling stations 34, 45, and 56. Those stations stretch generally in a northeasterly direction from the plant outfall and are 175 meters or so distant from each other. As can be seen from the data reported in Tables 34 and 35, the concentration of aromatic hydrocarbons (recorded maximum) decayed from 62.1 to 1.9 micrograms/L (ppb) over a distance of approximately 350 meters. Assuming an average concentration of aromatic hydrocarbons of 5 milligrams/liter (ppm) at the outfall, it can be estimated that at Station 56 (approximately 500 meters distant from the outfall), the effluent is diluted by a factor of 2600. Similarly, it can

TABLE 33. AROMATIC HYDROCARBONS IN PORT VALDEZ: VERTICAL DISTRIBUTION, JUNE 1980 STUDY

Sampling Date: June 6, 1980

Sampling Site: Westerly boundary line of diffusion zone, Station 42 (Colonell)

Depth (m)	Temperature (°C)	Total Aromatic Hydrocarbons (μg/L)	Benzene (μg/L)	Toluene (μg/L)	Xylenes (μg/L)
40	4.5	0.5	0.27	-	0.25
50	4.7	126.6	56.6	51.3	18.7
60	4.5	9.9	4.0	3.5	2.4
70	4.5	0.0	0.0	0.0	0.0

calculated that the permissible level (10 micrograms/L) for aromatic hydrocarbons is reached at a point 350 to 400 meters distant from the plant outfall.

As can be seen from the reported data, the centerline of the trap zone (near the mixing zone) in June 1980 was at a depth of approximately 50 meters. This was 15 to 20 meters shallower than the centerline of the trap zone observed during the September 1979 study, when the centerline was found at 60- to 70-meter depths. The shift in the position of the centerline is probably due to the increase in thickness of the surface layer as the summer progresses.

The outfall for treated effluent is designed to maximize mixing and dilution of the effluent with ambient water of the fjord. The diffuser consists of a 60-meter-long pipe that is provided with ten 10-cm-diameter and ten 12.7-cm-diameter ports spaced 3.05 meters apart on alternate sides of the pipe. The diffuser is located 65 to 75 meters below the surface of Port Valdez, approximately 275 meters from the shore. Treated effluent is discharged through these ports as turbulent jets, providing for highly efficient mixing of the effluent and ambient water over a horizontal distance of approximately 60 meters. The density of the effluent is normally less than the density of ambient water, so the effluent forms a buoyant plume that rises toward the surface, entraining heavier sea water until it reaches neutral buoyancy. At the depth of natural buoyancy, the plume spreads horizontally across the fjord, creating a submerged pancake of diluted effluent.

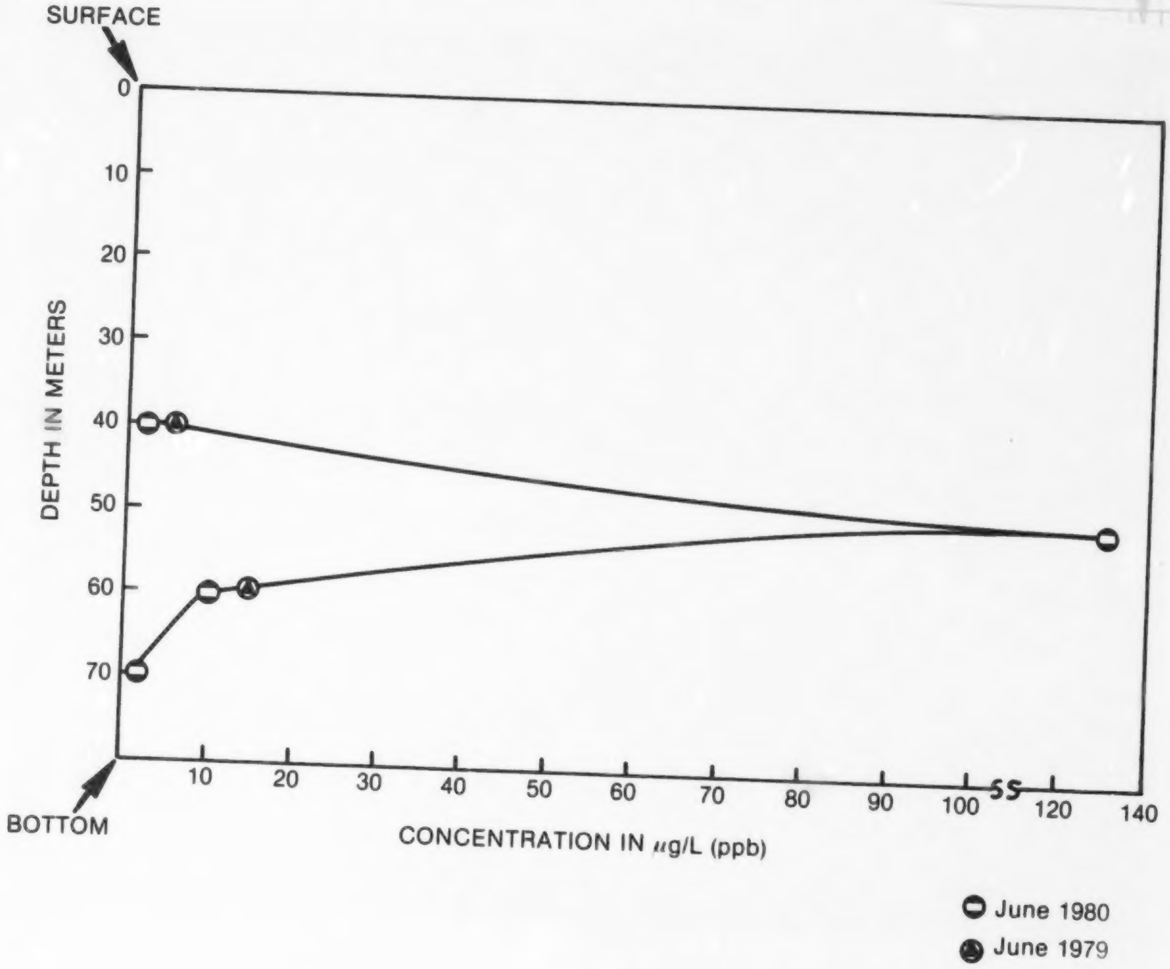

Figure 10. Decay of aromatic hydrocarbons in vertical plane, Station 42, Port Valdez, Alaska.

TABLE 34. AROMATIC HYDROCARBONS IN PORT VALDEZ: HORIZONTAL CONCENTRATION DECAY, JUNE 1980 STUDY

(Sampling Dates: June 3-12, 1980)

Station No. (Colonell)	Distance from Plant Outfall (m)	Sampling Depth (m)	Temp. (°C)	Maximum Concentration Total Aromatic Hydrocarbons (μg/L)	Maximum Concentration Benzene (μg/L)	Maximum Concentration Toluene (μg/L)	Maximum Concentration Xylenes (μg/L)
34	150	47	4.7	62.1	25.7	23.1	13.3
45	313	60	4.6	26.1	11.1	10.3	4.7
56	485	70	4.7	1.9	0.8	-	1.1

Conclusions

Studies carried out in June and September 1979 and in June 1980 indicate that the treated effluent discharged from the terminal facility (as measured by its aromatic hydrocarbon content) does not mix uniformly throughout the full vertical extent of the water column of the receiving waters of Port Valdez during the summer period of density stratification. During these times the volume of the mixing zone is grossly underutilized, and no significant amount of hydrocarbons appear to penetrate vertically into the surface layer. The surface layer, at certain periods, extends downward to the depth of the diffuser.

The aromatic hydrocarbons are contained just below the surface layer in a thin (vertically) pancake, spreading in a horizontal plane as far as 2 to 3 km from the mixing zone into Port Valdez. The vertical position of the pancake is near the bottom in the vicinity of the diffuser (0 to 10 m above the diffuser) during the late summer months. In the early summer months the pancake is located at a depth of approximately 50 meters, or 15 to 25 m above the depth of the diffuser.

Optimization of diffuser design must take into consideration not only the characteristics of the effluent and the receiving water, but also the prevailing hydrological conditions in the receiving water.

TABLE 35. AROMATIC HYDROCARBON PROFILE IN PORT VALDEZ, JUNE 1980 STUDY
(Sample Dates: June 3-12, 1980)

Station No. (Colonell)	Direction and Distance from the Outfall (m)	Sampling Depth (m)	Concentration (micrograms/liter)			
			Total Aromatic Hydrocarbons	Benzene	Toluene	Xylenes
34	NE, 150	40	27.9	8.1	9.0	10.8
		50	62.1	25.7	23.1	13.3
		60	0.0	0.0	0.0	0.0
		70	0.0	0.0	0.0	0.0
		80	0.0	0.0	0.0	0.0
45	NE, 313	30	0.0	0.0	0.0	0.0
		40	10.9	4.7	4.2	2.0
		50	1.2	0.5	0.0	0.7
		60	26.1	11.1	10.3	4.7
56	NE, 485	40	0.0	0.0	0.0	0.0
		50	0.6	0.4	0.0	0.2
		60	0.8	0.4	0.0	0.4
		70	1.9	0.8	0.0	1.1
42	NW, 175	40	0.5	0.25	0.0	0.25
		50	126.6	56.6	51.3	18.7
		60	9.9	4.0	3.5	2.4
		70	0.0	0.0	0.0	0.0

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APPENDIX A

ANALYTICAL SCHEME FOR ORGANIC MATERIAL BALANCE IN OILY WASTEWATERS*

INTRODUCTION

In order to characterize fully the chemical composition of oily wastewaters, three states of organic matter must be addressed: volatile, nonvolatile dissolved, and nonvolatile suspended.

The sum of these corresponds to the total organic content or total organic load of water, and is necessary for studying process efficiencies where material balance information is required.

To meet the objectives of this study -- determination of the effectiveness of organic load reduction by various units of modern oily wastewater treatment plant, and characterization of compositional changes induced by the process -- an analytical scheme was devised. The scheme is based on a procedure described in Advances in Chemistry: Petroleum in Marine Environment (A-1).

Two water samples are required for implementation of this scheme. One sample is used for determination of volatile organic content, and for characterization of dissolved nonvolatile organic fraction. The second sample is used for determination of total nonvolatile organic content. The analytical scheme is shown in Figure A-1.

One of the water samples is sparged by a stream of nitrogen, and volatile fraction is collected on an activated charcoal cartridge. The volatiles are extracted into carbon disulfide and analyzed gas-chromatographically. The acidified and sparged water sample is then Millipore-filtered (0.45-micron filter size) and analyzed for total nonvolatile organic carbon. A portion of the filtrate is extracted into chloroform and a portion is adsorbed on macroreticular resin (Amberlite XAD-7) and then re-desorbed into methanol. The Amberlite XAD-7 separated fraction contains highly polar organic materials (such as phenolic and carboxylic acids), while the chloroform-extractable fraction contains organic matter of intermediate polarity. Both fractions are profiled by the HPLC analysis.

A second water sample is acidified, sparged with nitrogen, ultrasonated (using an ultrasonic probe), and analyzed for total nonvolatile organic carbon. A value obtained for dissolved nonvolatile organic carbon is subtracted

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* By Ihor Lysyj, Rockwell International, Newbury Park, California.

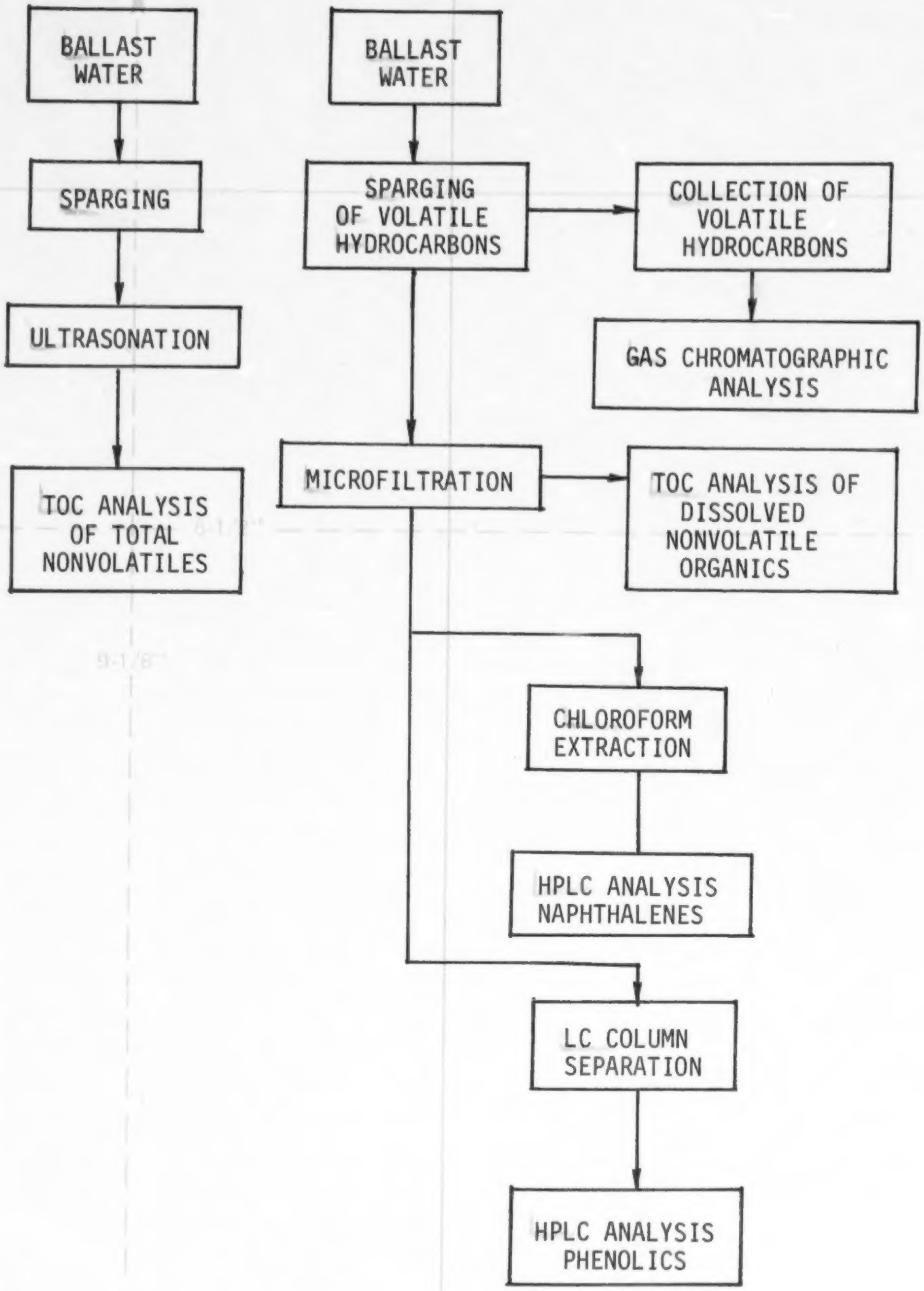
BALLAST WATER
SPARGING
ULTRASONATION
TOC ANALYSIS OF TOTAL NONVOLATILES
BALLAST WATER
SPARGING OF VOLATILE HYDROCARBONS
COLLECTION OF VOLATILE HYDROCARBONS
GAS CHROMATOGRAPHIC ANALYSIS
MICROFILTRATION
TOC ANALYSIS OF DISSOLVED NONVOLATILE ORGANICS
CHLOROFORM EXTRACTION
HPLC ANALYSIS NAPHTHALENES
LC COLUMN SEPARATION
HPLC ANALYSIS PHENOLICS

Figure A-1. Protocol for analysis of ballast water.

from the total nonvolatile organic carbon, providing the value for suspended organic carbon.

Implementation of this analytical protocol provides the following information:

1. Total organic load of the sample (the sum of three states of organic matter in the sample)
2. Total volatile organic content (a sum of all gas-chromatographically characterized compounds)
3. Total dissolved nonvolatile organic content of the sample (the value of TOC on the Millipore-filtered sample)
4. Total suspended organic content (the difference between total nonvolatile TOC and dissolved nonvolatile TOC)

Additionally, in greater detail are characterized:

1. Volatile organic compounds by means of gas-chromatographic analysis
2. Dissolved nonvolatile, highly polar organic compounds by means of HPLC analysis of Amberlite XAD-7 separated fraction
3. Dissolved nonvolatile intermediate-polarity organics by means of HPLC analysis after separation by liquid-liquid extraction into chloroform

Procedural details of this scheme follow.

VOLATILE ORGANIC FRACTION

Volatile organic compounds found in oily wastewaters consist primarily of lower molecular weight aliphatic and aromatic hydrocarbons. Because of its relatively high vapor pressure, this fraction is quite often lost during analysis of oily wastes. For this reason a separate procedural step was incorporated into the overall scheme for analysis of volatile fraction. An unfiltered sample of oily wastewater is used in this determination. The volatile fraction is separated from water by means of nitrogen sparging and collected in an activated carbon absorption column. The collected compounds are desorbed into carbon disulfide and analyzed gas-chromatographically.

The sparging apparatus consists of a glass vessel and the head. The head of the sparging assembly consists of a rubber stopper or a jar lid, into which a gas dispersion tube and adsorption train are inserted. The collection assembly consists of drying tube (6-mm-ID by 13-cm-long glass tube filled with 10/20 mesh Drierite) and charcoal tube (NIOSH-approved for determining organic vapors in air, obtainable from Supelco or MSA). A 2-liter, round-bottom flask was used as a sample vessel in the laboratory study of accuracy of the method. In the field work, however, glass jars used for sampling were equipped with a sparging head, and volatile organics were sparged directly from the sampling container.

Nitrogen is purged through the sample at 500 ml/minute for a period of 30 minutes. The charcoal tube is in two sections to ensure complete trapping. The total capacity of the charcoal section is approximately 15 mg of hydrocarbons (this would correspond to a 1-liter sample containing 15 ppm hydrocarbons).

Activated carbon cartridges are opened after the sparging operation and the front and back portions of carbon are transferred into vials equipped with a Mininert valve seal. One milliliter of carbon disulfide is introduced through the septum by means of a syringe (to prevent losses of volatiles due to heat of adsorption). The vials are allowed to stand at room temperature for 30 minutes with periodic shaking. A 1-microliter aliquot is withdrawn and injected into the gas chromatograph.

The analysis of separated volatile fraction can be carried out using a number of gas-chromatographic columns under various conditions including those described in Standard Test Method ANSI/ASTM D 2267-68. The following conditions were used in the laboratory studies:

GC column:	3% OV-101 on 100/120-mesh Chromosorb G-HP, 3.66 m long by 32 mm diameter stainless steel
Column temperature:	1.5 minutes hold at 60°C, temperature-programmed at 10°C/minute to 120°C
Detector:	Hydrogen flame ionization

During the field studies a simpler isothermal Gow-Mac gas chromatograph equipped with a hydrogen flame ionization detector was used. A 3.66-meter-long by 32-mm-diameter column packed with 5% OV-17 substrate on Chromosorb G-HP was used for separation at 80°C with a 20-ml/minute flow of carrier gas.

NONVOLATILE DISSOLVED ORGANIC FRACTION

The acidified and sparged water sample is Millipore-filtered using a Type HA 0.45-micron filter. This operation separates dissolved organic matter from suspended materials. (Some batches of Type HA Millipore filters produce significant blank values, and it is recommended that each batch used should be checked out by filtering and analyzing the distilled water.)

The total organic carbon (TOC) is determined on an acidified, nitrogen-sparged and Millipore-filtered water sample. The analysis is performed according to the procedure described in *Standard Methods for Examination of Water and Wastewater*, Method 505 (Ref. 8-2). Potassium acid phthalate solution is used for multipoint calibration of the instrument. The results are expressed in mg/L. They correspond to the quantity of dissolved, nonvolatile organic carbon present in the sample.

The chemical composition of dissolved, nonvolatile organic fraction is characterized by high-pressure liquid chromatography (HPLC) in greater detail after separation from the water.

There are a number of methods for separating dissolved organic matter from the water. We have found, however, that none of the different methods of separation (alone) can provide for total recovery of all organic compounds that might be present in the oily waters. For example, liquid-liquid extraction (using chloroform) provides for satisfactory separation for organic compounds of intermediate polarity, but not for highly polar compounds such as polyhydrobenzenes. The macroreticular resins (such as Amberlite XAD-7), on the other hand, effectively separate polar compounds, but were found to be ineffective for separation of compounds such as naphthalenes. For these reasons, it was decided to use both liquid-liquid extraction and macroreticular resins for the separation of dissolved organic matter from oily wastewater samples.

Separation

The acidified, sparged, and Millipore-filtered water sample is divided into two aliquots. One is used for liquid-liquid extraction, the other for macroreticular resin separation.

The liquid-liquid extraction is carried out in a 1-liter separating funnel. Three 50-ml volumes of chloroform are used successively. The chloroform extracts are combined and reduced in volume to 5 ml or less in a Kuderna-Danish evaporator.

The accumulator column separation method is similar to a method described by Junk (Ref. A-3). The apparatus consisted of a 1-liter-reservoir bulb connected to a 140-mm Amberlite XAD-7 column equipped with a stopcock. The separation of organics from the water sample is accomplished by rinsing the column with 25 ml of methanol (under gravity flow), followed by introduction of the water sample into a 1-liter-reservoir bulb and letting the sample pass through the column under the gravity flow. The retained organics are then desorbed into 25 ml of methanol. Extracts are usually reduced to 1 or 2 ml by evaporation with flowing nitrogen at room temperature, or in Kuderna-Danish evaporators.

Special pretreatment of commercially available Amberlite XAD-7 resin is necessary to overcome the problem of high blank values. Fines are removed by slurrying the resin in methanol and decanting. Then the impurities present in the resin are extracted by refluxing the resin in the Soxhlet apparatus for 8 hours each with methanol, acetonitrole, and diethyl ether. The purified resin is introduced as a slurry into a glass column 140 mm long by 8.5 mm internal diameter. Accumulator columns are always stored filled with methanol.

Separated and concentrated fractions (liquid-liquid extracted and macroreticular-resin-separated) containing dissolved nonvolatile organics are analyzed using the HPLC procedure.

Analysis

The aromatic content of oily wastewater is of toxicological significance, and the analytical procedure was devised to provide chemical characterization of this fraction. The analysis is carried out under conditions specified in Table A-1. Aromatic compounds elute in order of polarity: phenolic materials in a 1- to 4-minute retention-time window, nitrogen heterocyclics in 4 to 8

TABLE A-1. CONDITIONS FOR HPLC ANALYSIS FOR CLASS CHARACTERIZATION OF AROMATIC COMPOUNDS

Instrument:	Spectra Physics HPLC Model 3500B
Column:	Partisil PXS/10/25 ODS-2, 25 cm, Whatman Corp.
Mobile Phase:	30% water, 70% methanol
Flowrate:	1.32 ml/minute, pressure 6,894,760 Pa
Sensitivity:	AUFS* - 0.16
Recorder Speed:	1.27 cm per minute
Sample Size:	10 microliters

* Absorption units full scale.

minutes, alkyl-benzenes in 6 to 14 minutes, and PAH after 14 minutes (Figure A-2). Detection and analysis of the elutants are performed using UV detection at a fixed absorption band of 254 nm. It was found that while the absorption characteristics of different aromatic compounds vary, there is a similarity in the intensity of UV responses within each of the specified groupings: alkyl-benzenes, phenolic compounds, and heterocyclics (Table A-2). Because of this, it is possible to establish an average UV response factor for each class of interest. The calculations are then performed by integrating the total area in each time window (0-4, 4-6, and 6-14 minutes, which corresponds to phenolics, heterocyclics, and aromatic compounds, respectively) and proportioning such areas to the respective group response factors. In this study, two analyses were performed: one for determination of naphthalene and derivatives, the other for determination of phenolic compounds. The chloroform extract procedure was used for quantification of naphthalenes, while phenolic compounds were quantified using the Amberlite XAD-7 method.

SUSPENDED ORGANIC FRACTION

The suspended organic matter in oily wastewater samples consists primarily of aliphatic hydrocarbons and other water-insoluble components of petroleum. It is usually defined as "the oil," and most of the standard methods for use in water analysis (Ref. A-2) are oriented toward quantification of this fraction of organic content that might be present in oily wastewater.

The following procedure is used for characterization of this fraction. The acidified and nitrogen-sparged water sample is ultrasonicated prior to analysis for TOC. The technique for ultrasonication of oil-in-water mixtures as developed by Gruenfeld (Ref. A-4) is used. An ultrasonic vibrator probe is immersed a few cm below the surface of the sample in the cylindrical vial, and

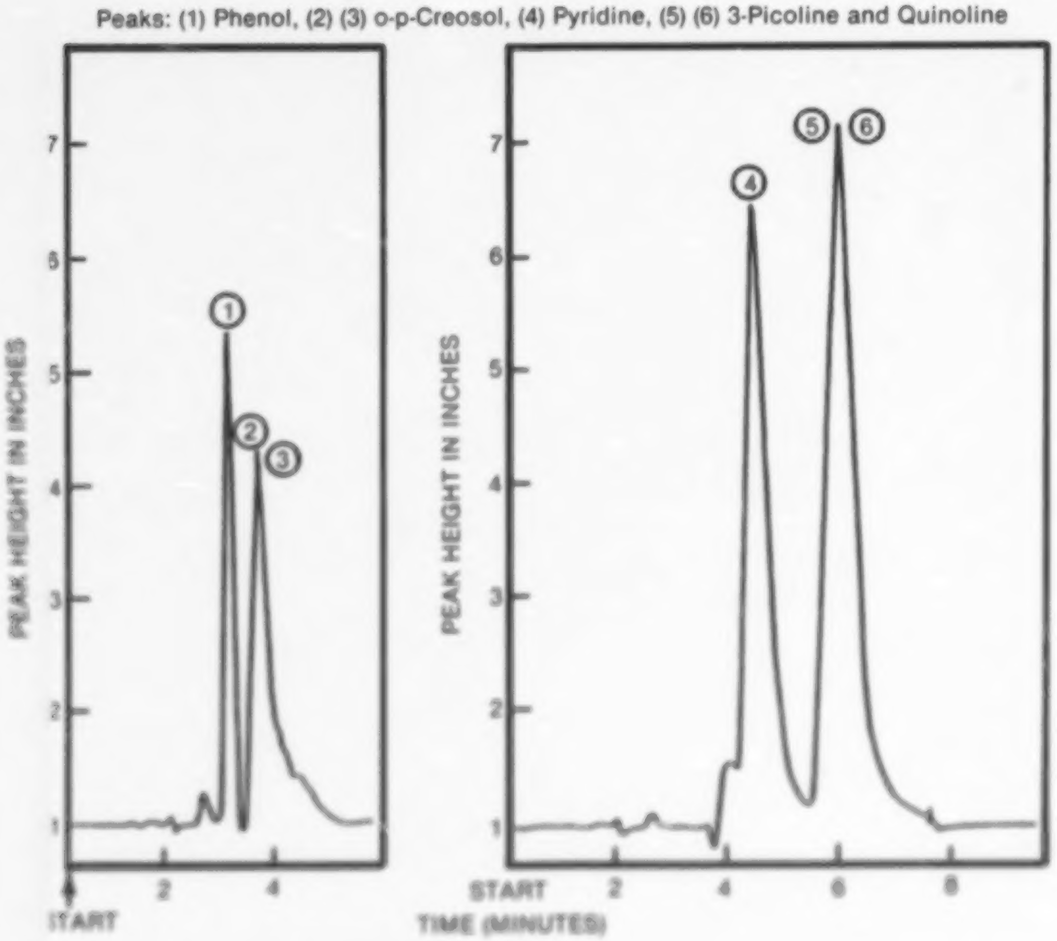

Figure A-2. HPLC calibration of phenolic and heterocyclic compounds. (1 inch = 2.54 cm)

the power to the probe is gradually increased from 0 to 300 watts. A Braunsonic Model 1510 probe manufactured by B. Braun, Mesungen, AG, was used in this work. It was found that the shape of the sample container is rather important to oil-in-water dispersion effectiveness. Best results were obtained in cylindrical vessels, the caps of which were lined with aluminum foil.

In narrow cylindrical vessels oily film forms in a relatively small surface area, and adheres to glass walls that are in close proximity to the ultrasonic probe tip. The aluminum foil from the sampling vessel lid is immersed into the sample and any oil that might adhere to it is re-suspended in the water by ultrasonation. The use of cylindrical vials for sampling and ultrasonic probes for dispersal leads to formation of stable emulsions (10 to 30 minutes). Reproducible aliquots of such emulsions are injected in the TOC analyzer and analyzed for total nonvolatile organic content in a standard procedural manner (Ref. A-2).

TABLE A-2. HPLC SEPARATION AND CALIBRATION DATA FOR PHENOLIC COMPOUNDS, NITROGEN HETEROCYCLICS, AND AROMATIC HYDROCARBONS*

Class	Compound	Retention Time in Minutes	Response µV-sec* (mg/L)	Class Factors µV-sec* (mg/L)
Phenolic	Pyrogallol Isomers	1.67; 2.21; 2.58	4,099	2,738
	Hydroquinone Isomers	2.34; 2.98	2,021	
	Resorcinol	2.45	2,012	
	Phenol	3.29	2,818	
Nitrogen Heterocyclics	Pyridine	4.48	15,723	13,637
	Quinoline	6.64	11,550	
Aromatic Hydrocarbons	Benzene	6.40	1,261	1,291
	Toluene	9.39	1,385	
	Xylenes	14.55	1,226	

*Hewlett-Packard Integrator, Model 3370A, was used.

The concentration of suspended organic matter is determined as the difference between the TOC of the sparged unfiltered sample and the sparged filtrate.

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APPENDIX B

QUALITY OF THE DATA*

INTRODUCTION

It is the funamental responsibility of an analytical operation to establish and maintain a continuing program to ensure the validity and reliability of the data being produced by the laboratory. Part of this responsibility is to select the proper analytical methods and the necessary quality control procedures for accurate measurement of required parameters.

The method selection approach was described in a recent publication by Ballinger (Ref. B-1) in the following manner:

> "The method should measure the required property or constituent with precision, accuracy, and specificity sufficient to meet the data needs of the EPA, in the presence of the interfering materials usually encountered in water and wastewater."

The key element of this statement is "sufficient to meet the data needs." Meeting the data needs, rather than some abstract perfection, is the object of analytical chemistry operations. In itself, no data is good or bad, but is of varying degrees of reliability and accuracy. In order to properly evaluate and interpret the generated data, it is necessary to know its reliability and accuracy. While determination of data validity is as old a practice as chemistry itself, the formalized procedures for performing checks on analytical procedures appeared only recently. The EPA is in the forefront of codification and implementation of formal quality control and quality assurance protocols. Under direction from the EPA Administrator, mandatory regulations regarding quality control and quality assurance requirements in all EPA grants, contracts, cooperative agreements, and interagency agreements became effective on June 14, 1979 (Ref. B-2). The instruction includes the following:

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* By Ihor Lysyj and Matthew Young, Rockwell International, Newbury Park, California.

QUALITY ASSURANCE REQUIREMENTS FOR ALL EPA EXTRAMURAL PROJECTS INVOLVING ENVIRONMENTAL MEASUREMENTS*

"Potential contractors/grantees shall provide the following quality assurance (QA) information and related documentation for EPA funding of any projects involving the collection and analyses of samples. These criteria shall be used in determining the overall acceptability of any contractor or grantee.

1. A written QA plan shall be developed that includes the oversight role of management, identification of personnel responsible for the QA program, proper sample collection, use of approved measurement techniques, calibration standards and their verification, internal quality control practices, and appropriate data management controls. Pre-award information can be limited to that required to evaluate capabilities. The specific QA plan may be developed and subsequently approved by EPA after award of funds.

2. An estimate of costs associated with the QA program in terms of percentage of overall project cost shall be provided. Normally, a minimum of 10% to 30% of the estimated sample collection and analyses costs will be necessary for adequate quality control.

3. As a condition of award, acceptable performance must be demonstrated on audit samples, when available and where applicable, and throughout duration of contract/grant.

4. Provision shall be made for on-site laboratory and/or field sites evaluation at option of the Project Officer for a performance evaluation and for documentation that all equipment and supplies necessary for successful completion of project are available.

5. Documented quality control performance will be submitted with the final report and otherwise as required by the Project Officer."

While those regulations became effective only after award of the contract for the program reported here, they were nevertheless closely followed in all sampling and analytical operations. Formal quality control procedures were developed and implemented during the operational phase of the program and a formal quality assurance audit was carried out. The quality assurance audit covered operation of the Rockwell EMSC laboratory in Newbury Pk., the Rockwell laboratory in Valdez, Alaska, and sampling operations on-site at the Alyeska terminal treatment facility in Valdez.

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* This includes, but is not limited to, grants, contracts, cooperative agreements, and interagency agreements.

QUALITY CONTROL

In fundamental terms, the object of quality control in an analytical chemistry operation is to assure the absence of false-positive and false-negative bias from the reported data and indicate the accuracy and precision of the reported data. False-positive values are normally recorded as a result of system contamination and interferences, while false-negative values are normally recorded as a result of incomplete recoveries.

The accuracy of a method is normally defined as a degree of agreement between measured value and the true value of a given parameter. As such, it is a function of false-negative and false-positive biases. The accuracy of the individual measurement is usually determined by analyzing a standard solution or spiking a sample with a known quality of material and re-analyzing. Determination of the method and field blanks are also considered as a function of accuracy. If such blanks exist in a given procedure, they are determined and compensated for in the calculation of results.

Precision is normally defined as the degree of agreement between repeated measurements of one property using the same method or technique. It is normally quantified as a "replicability" and expressed as standard deviation measuring the variability of replicate runs.

A quality control protocol was established for all of the analytical operations carried out on-site in Valdez, Alaska, and off-site in Newbury Park, California, and implemented during the Summer 1978, Winter 1979, and Summer 1979 field studies.

Sample Collection

A set of samples was collected at each selected point of the process stream each day of field operations. Individual samples were collected for oil and grease analysis, TOC determination, and volatile and nonvolatile dissolved fractions characterization. Analysis of samples was initiated usually within 1 hour of collection, and completed on the same day. Samples awaiting analysis were stored in a refrigerator. Extracts of the samples destined for off-site analysis (HPLC characterization of dissolved nonvolatile fraction) were also stored in a refrigerator.

Volatile Organic Fraction

The volatile organic fraction in treated and untreated ballast water consists of lower molecular weight hydrocarbons primarily of an aromatic nature. They are determined by the gas-chromatographic procedure described in Appendix H.

Blank determinations were made daily by injecting solvent (carbon disulfide) into the gas chromatograph and performing the analysis in a normal manner. Triplicate determination of blank values was made. An example of a procedural blank as recorded during the August 9, 1978 operation is shown in Figure B-1.

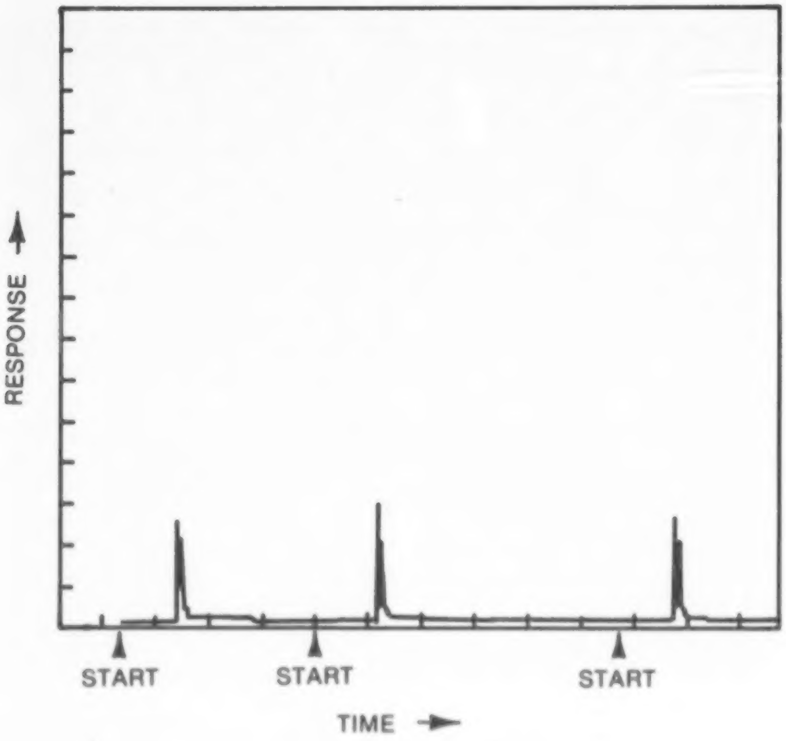
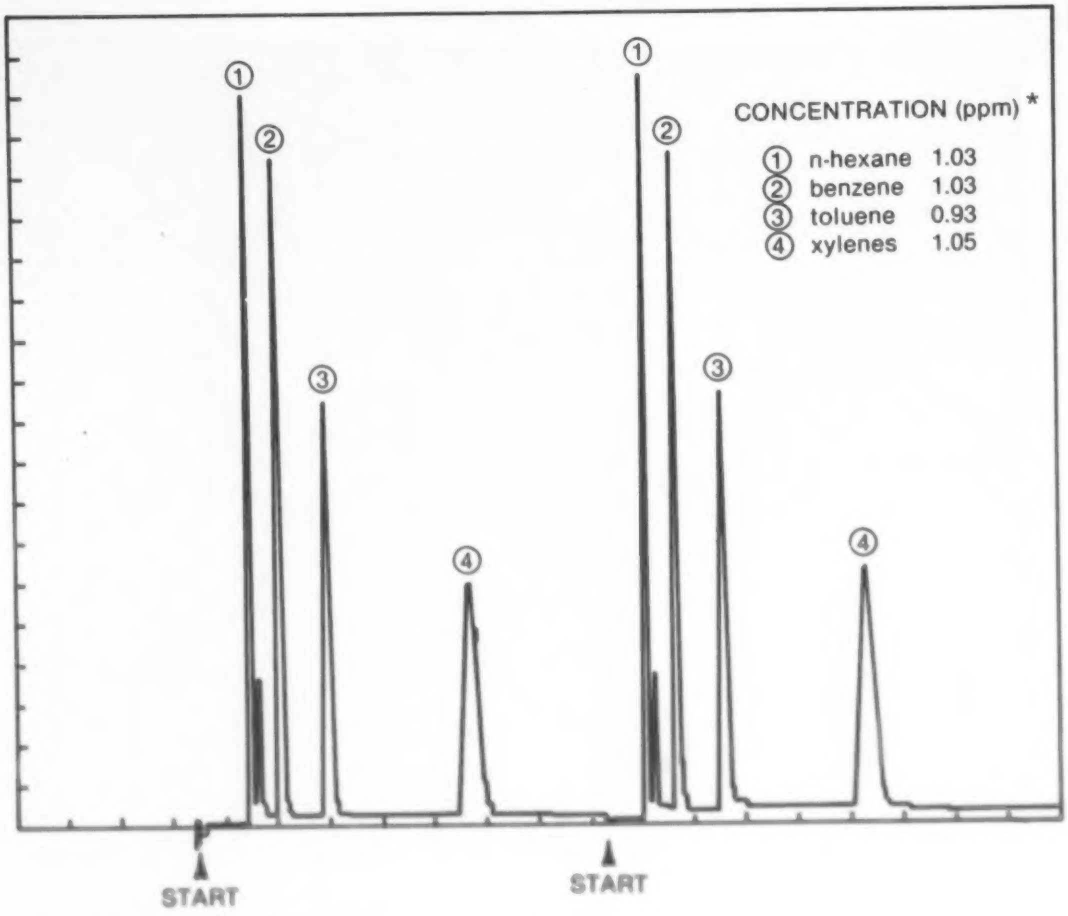


Figure B-1. Determination of gas-chromatographic instrumental blank (repetitive solvent injections)

Calibration of the instrument was also performed daily. The instrument was calibrated for n-hexane (a model compound for volatile aliphatic hydrocarbon), benzene, toluene, and xylenes. Organic solvent concentrates were used in this operation. The practical operational range of the procedure was defined as 0.1 ppm to 3 ppm for concentration of each hydrocarbon. Four-point calibration covering this range was carried out. The calibrating points selected were in 0, 0.5, 1.0, and 3.0 ppm concentration ranges. Duplicate or triplicate determinations were performed at each calibration point. An example of replicate analysis of calibrating solutions performed on August 9, 1978, is shown in Figure B-2. Tabulation of calibrating data is reported in Table B-1.

Calibration data was tabulated and plotted each day and used for calculation of results only on that day of operation. An example of calibration curves for n-hexane, benzene, toluene, and xylenes for instrument operation on August 9, 1978, is shown in Figure B-3.

Replication. Each analysis for volatile organic fraction was performed in triplicate (three separate injections of the solvent extracts) and the average value was reported. A typical triplicate analysis of treated ballast effluent as recorded on August 9, 1978, is reproduced in Figure B-4. Calculations are reported in Table B-2.



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* Equivalent concentrate to aromatic hydrocarbon content in water sample

Figure B-2. Replicate analysis of calibrating solution, August 9, 1978.

Accuracy. Accuracy of the procedure was determined by adding known amounts of volatile hydrocarbons to synthetic sea water and analyzing the resulting solutions following the procedure described in Appendix H. This was done by introducing known volumes of aromatic hydrocarbons into 850 ml of synthetic sea water, sparging the mixture with nitrogen, and executing all procedural steps in the same manner as if the unknown water sample were analyzed. The synthetic sea water was made using "Instant Ocean" salt mixture (obtained from Aquarium Systems, 33208 Lakeland Blvd., Eastlake, Ohio 44094). The results are reported in Table B-3. It was established that the average recovery, and subsequent accuracy for volatile hydrocarbons in the low-ppm concentration range, was 94.5% with ±5% standard deviation.

Precision. The precision of the method was determined as reproducibility of multiple analyses of 10 samples of actual treated bilgewater. The results shown in Table B-4 indicate a relative standard deviation of ±1.6% for benzene,

TABLE B-1. CALIBRATION DATA, GAS CHROMATOGRAPH, AUGUST 9, 1978

Compound	Concentration,* ppm	Response (Integral Count)	Average Response (Integral Count
n-Hexane	0	0	0
	0	0	
	0.52	105	103
	0.52	100	
	1.03	177	175
	1.03	173	
	3.09	380	374
	3.09	368	
Benzene	0	0	0
	0	0	
	0.52	120	121
	0.52	122	
	1.03	220	220
	1.03	220	
	3.09	488	484
	3.09	480	
Toluene	0	0	0
	0	0	
	0.47	125	124
	0.47	123	
	0.93	220	218
	0.93	215	
	2.79	512	511
	2.79	510	
Xylene	0	0	0
	0	0	
	0.53	143	139
	0.53	135	
	1.05	275	267
	1.05	258	
	3.14	640	640
	3.14	640	

* Equivalent concentrate to aromatic hydrocarbon content in water samples.

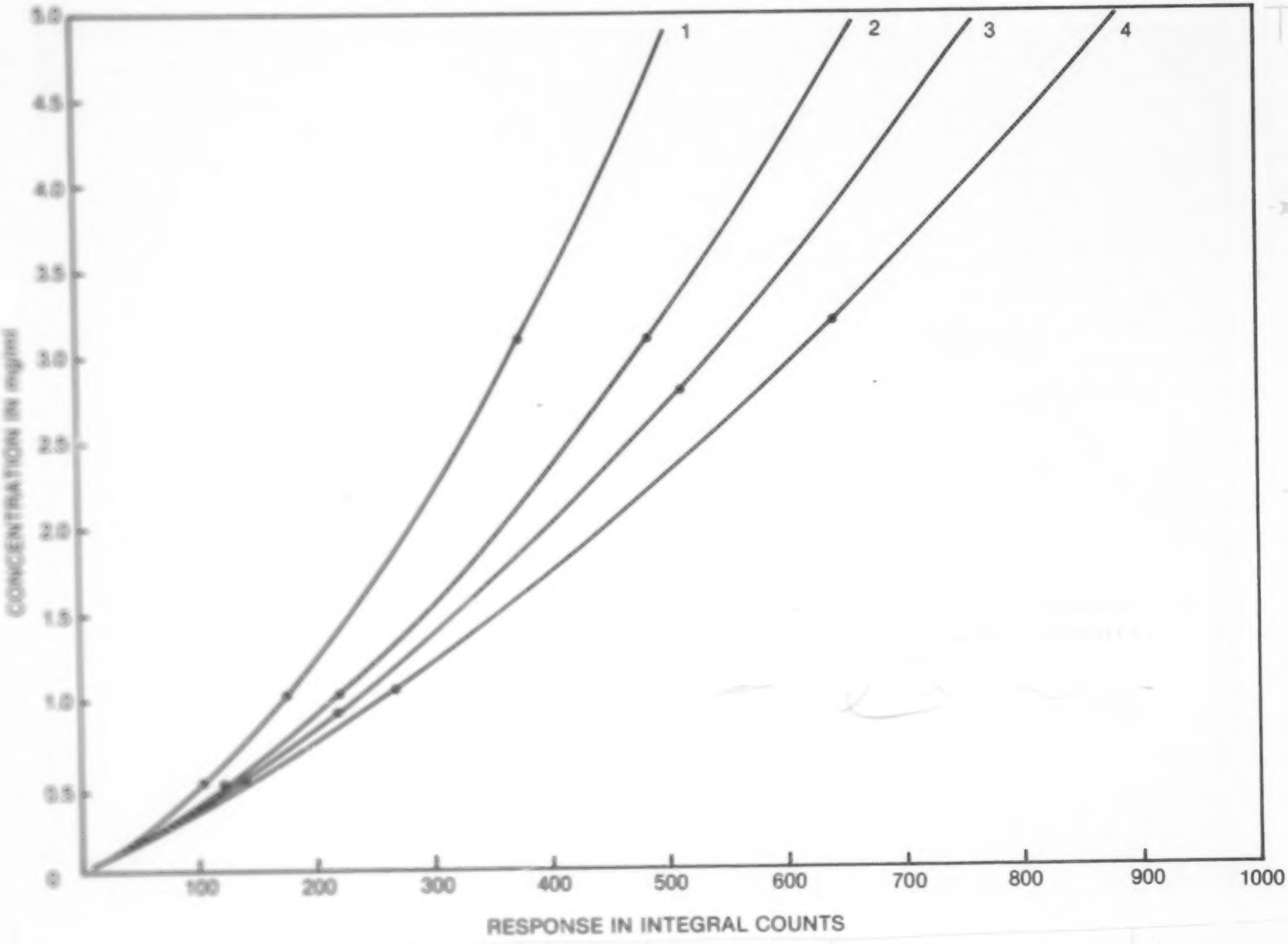

Figure B-3. Calibration curve for volatile organic fraction: (1) n-hexane, (2) benzene, (3) toluene, (4) xylenes.

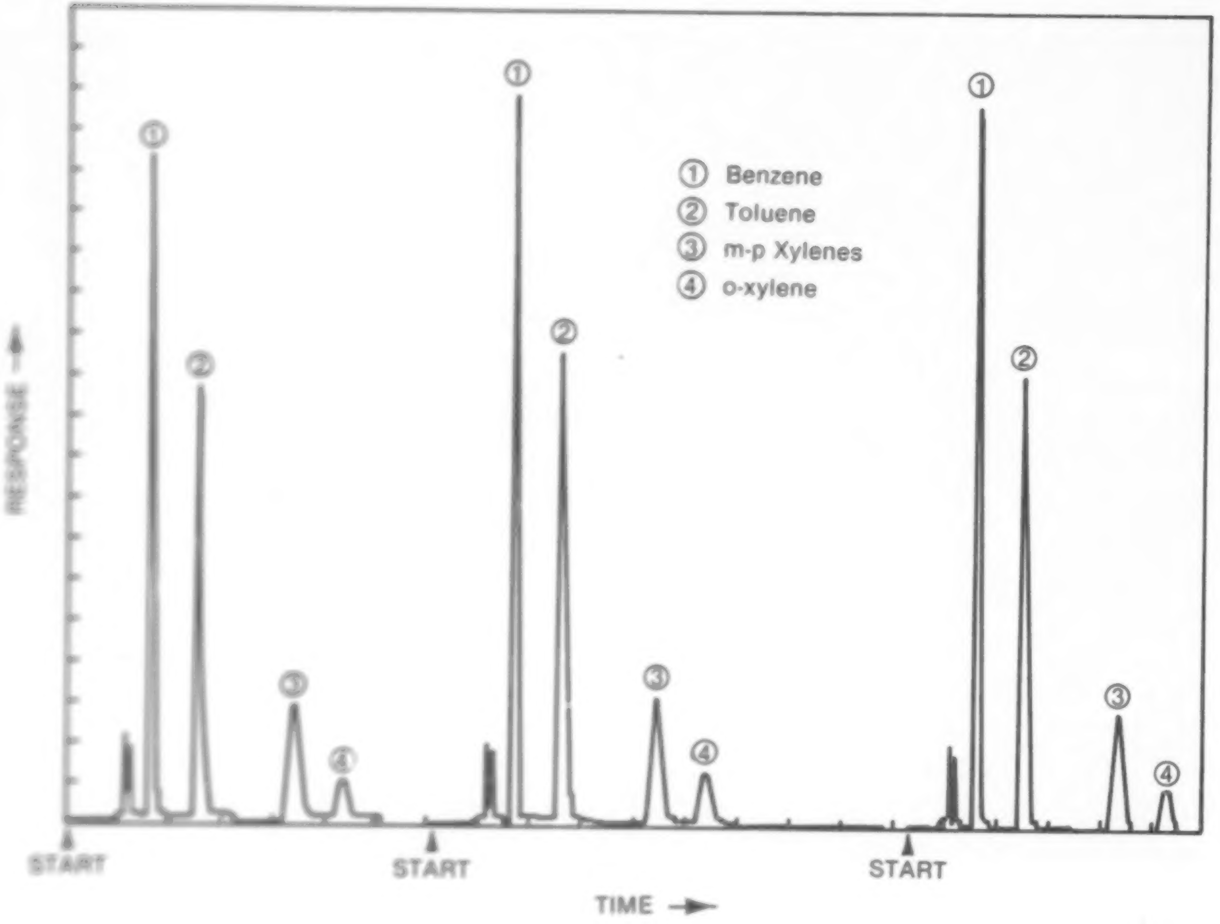

Figure B-4. Triplicate analysis of volatile fraction in treated ballast, August 9, 1978.

TABLE B-2. VOLATILE AROMATIC HYDROCARBONS IN TREATED BALLAST EFFLUENT, AUGUST 9, 1978

Compound	Response (Integral Count)	Concentration (Uncorrected Value), mg/L	Concentration (Corrected for Volume Value), mg/L
Benzene	248		
	255		
	251		
Average	251	1.2	1.5
Toluene	240		
	260		
	244		
Average	248	1.1	1.4
Xylenes	152		
	170		
	138		
Average	153	0.6	0.8

±1.7% for toluene, and ±5.0% for xylenes.

Verification of Hydrocarbon Identity. The identity of peaks corresponding in retention time to benzene, toluene, and m-xylene was confirmed mass-spectrometrically. Mass spectra were generated for peaks with retention times corresponding to standard benzene, toluene, and m-xylene. The comparison of standard and unknown spectra indicated that principal aromatic compounds of treated ballast water are indeed benzene, toluene, and xylenes. Because m- and p-xylenes, ethylbenzenes have similar mass spectra and R.T., no distinction of these compounds was made. The computer Probability-Based Matching (PBM) technique was also used for confirmation of peak identities.

Independent Method Comparison. During the Winter 1979 study all samples of treated effluent were analyzed independently by Rockwell International, contractor for the EPA, and Radian Corporation, contractor for the Alyeska Pipeline Service Company. Effluent samples were collected simultaneously during 10 days of the Winter 1979 study and analyzed by Rockwell personnel using the procedure described in Appendix C (analysis based on activated carbon adsorption) and independently by Radian personnel using the EPA priority pollutant protocol procedure (Ref. B-2) (analysis for purgeable volatile compounds based on Tenax GC adsorption). Separate samples were collected by the two contractors each day during 10 days of plant study. The results, shown in Table B-3, indicate satisfactory checks on two different methods of analysis for volatile hydrocarbons.

TABLE B-3. ACCURACY AND RECOVERY OF VOLATILE HYDROCARBONS FROM SYNTHETIC SEA WATER SOLUTIONS

Compound	mg Present	mg Recovered	% Recovery
Benzene	0.88	0.86	97.7
Toluene	0.87	0.84	96.6
Xylenes	0.86	0.90	104.7
Benzene	1.76	1.64	93.2
Toluene	1.73	1.56	90.2
Xylenes	0.86	0.74	86.0
Benzene	1.76	1.80	102.3
Toluene	1.73	1.68	97.1
Xylenes	0.86	0.80	93.0
Benzene	1.76	1.58	89.8
Toluene	1.73	1.52	87.9
Xylenes	0.86	0.74	86.0
Benzene	1.76	1.69	95.9
Toluene	1.73	1.68	97.1
Xylenes	0.86	0.77	89.8
Benzene	1.76	1.70	96.4
Toluene	1.73	1.70	98.3
Xylenes	0.86	0.82	95.0
Benzene	1.76	1.71	97.3
Toluene	1.73	1.70	98.1
Xylenes	0.86	0.81	93.8

Mean % Recovery and Relative Standard Deviation

Benzene	96.1 ±3.9
Toluene	95.0 ±4.2
Xylenes	92.6 ±6.4

TABLE B-4. REPRODUCIBILITY OF ANALYSIS - BENZENE, TOLUENE, XYLENES - DEVIATIONS FROM AVERAGE VALUE OF MULTIPLE ANALYSIS OF EXTRACTS OF TREATED EFFLUENT

% Benzene	% Deviation	% Toluene	% Deviation	% Xylenes	% Deviation
100.0	0	100.0	0	78.2	-21.8
98.2	-1.8	105.6	+5.6	112.2	+12.2
101.8	+1.8	94.4	-5.6	109.6	+ 9.6
99.6	-0.4	95.2	-4.8	98.0	- 2.0
100.0	0	100.4	+0.4	98.0	- 2.0
99.6	-0.4	102.6	+2.6	103.0	+ 3.0
100.0	0	101.5	+1.5	100.5	+ 0.5
98.8	-1.2	96.8	-3.2	99.3	- 0.7
101.6	+1.6	104.8	+4.8	111.1	+11.1
100.0	0	98.4	-0.6	90.2	- 9.8
99.5	-0.5	96.6	-3.4	104.3	+ 4.3
101.0	+1.0	103.7	+3.7	102.4	+ 2.4
100.0	0	99.2	-0.2	93.7	- 6.3
99.5	-0.5	100.8	+0.8		
101.2	+1.2	100.3	+0.3	103.0	+ 3.0
98.8	-1.2	99.7	-0.3	95.0	- 5.0
100.0	0			102.5	+ 2.5
98.3	-1.7	98.5	-1.5	97.5	- 2.5
101.3	+1.3	101.5	+1.5	104.6	+ 4.6
100.4	+0.4	100.2	+0.2	97.5	- 2.5
100.4	+0.4	100.0	0	100.3	+ 0.3
99.6	-0.4	99.7	-0.3	99.7	- 0.3
99.2	-0.8	98.4	-1.6	100.0	0
102.5	+2.5	102.9	+2.9	106.6	+ 6.6
98.3	-1.7	98.6	-2.4	93.4	- 6.6
97.0	-3.0	95.6	-4.4	95.5	- 4.5
95.0	-5.0	96.9	-3.1	100.6	- 0.6
102.4	+2.4	103.1	+3.1	96.6	- 3.4
98.3	-1.7	102.2	+2.2	109.6	+ 9.6
107.7	+7.7	102.2	+2.2	97.8	- 2.2
99.2	-0.8	100.3	-0.3	98.5	- 1.5
97.6	-2.4	97.5	-2.5	101.0	+ 1.0
103.4	+3.4	101.9	+1.9	100.5	- 0.5
Standard Deviation	±1.6		±1.7		±5.0

Combined aromatic hydrocarbon prevision: standard relative deviation = ±2.8

Relative standard deviation = $\sqrt{\frac{\Sigma d^2}{n-1}}$ where d is % deviation and n = number of observations.

TABLE B-5. AROMATIC HYDROCARBON ANALYSIS, COMPARISON BETWEEN EPA PRIORITY POLLUTANT PROTOCOL (GC-MS) AND ROCKWELL'S FIELD PROCEDURE, WINTER 1979 STUDY (MEAN VALUES)*

	Radian (GC-MS)	Rockwell (Field Method)
Benzene	2.6 ppm	2.1 ppm
Toluene	1.7 ppm	1.9 ppm
Xylenes/Ethylbenzene	0.98 ppm	1.0 ppm

* 10 determinations.

Instrument Performance Consistency. A record of calibration data was maintained for each day of field operations and a comparison was made of daily variations in instrument response. The calibration data generated during the 10 days of the Summer 1978 study is reported as an example of instrument performance consistency in Table B-6. As the reported data indicates, the gas chromatograph performed consistently without any drift in response. The response varied from day to day approximately ±4%.

Suspended and Dissolved Nonvolatile Fraction

The TOC procedure described in Appendix A was used for determination of nonvolatile organic load of the ballast water.

Blank determinations were made daily by injecting distilled water into a Beckman TOC analyzer and performing analyses in a normal manner. The blank determination was performed until consecutively reproducible triplicates were obtained. An example of a procedural blank as recorded during the August 9, 1978, operation is shown in Figure B-5.

Calibration of the Beckman TOC analyzer was also performed daily. The instrument was calibrated using a standard solution of potassium acid phthalate. Three or more point calibration was carried out in the 0 and 25 mgC/L concentration range. Triplicate determination was performed at each calibration point. An example of replicate analysis of calibrating solutions performed on August 9, 1978, is shown in Figure B-5. Tabulation of the calibrating data is reported in Table B-7.

Calibration data was tabulated and used only during the same day for calculation of results. An example of the calibration curve is shown in Figure B-6.

Replication. Each TOC analysis was performed in triplicate and the average value was reported. Three separate aqueous samples were injected into the TOC analyzer and analyzed in a manner described in Appendix A. A typical triplicate analysis of Millipore-filtered and ultrasonated unfiltered ballast water

TABLE B-6. INSTRUMENT PERFORMANCE CONSISTENCY

	n-Hexane Concentration (mg/L)			Benzene Concentration (mg/L)		
	0.52	1.03	3.09	0.52	1.03	3.09
Date	Average Response In Integral Count			Average Response In Integral Count		
8-7-78	-	176	428	-	192	507
8-8-78	110	186	383	142	241	520
8-9-78	103	175	374	121	220	487
8-10-78	110	174	370	130	221	516
8-11-78	113	186	387	136	227	513
8-12-78	110	184	400	138	223	504
8-13-78	115	177	369	133	219	506
8-14-78	112	173	376	133	219	491
8-15-78	115	165	377	120	212	525
8-16-78	108	175	376	135	226	517
Average Response and Standard Deviation	111 ±6	177 ±7	384 ±18	132 ±7	220 ±12	509 ±12

	Toluene Concentration (mg/L)			Xylenes Concentration (mg/L)		
	0.47	0.93	2.79	0.53	1.05	3.14
Date	Average Response In Integral Count			Average Response In Integral Count		
8-7-78	-	220	544	-	280	624
8-8-78	139	242	541	156	283	675
8-9-78	124	218	511	139	267	640
8-10-78	122	218	500	135	249	654
8-11-78	131	233	530	148	272	680
8-12-78	128	221	520	143	273	700
8-13-78	124	218	519	135	253	665
8-14-78	125	218	508	132	257	651
8-15-78	120	212	525	128	247	652
8-16-78	128	221	517	136	254	656
Average Response and Standard Deviation	127 ±5.6	222 ±9	522 ±14	139 +9	264 ±13	660 ±21

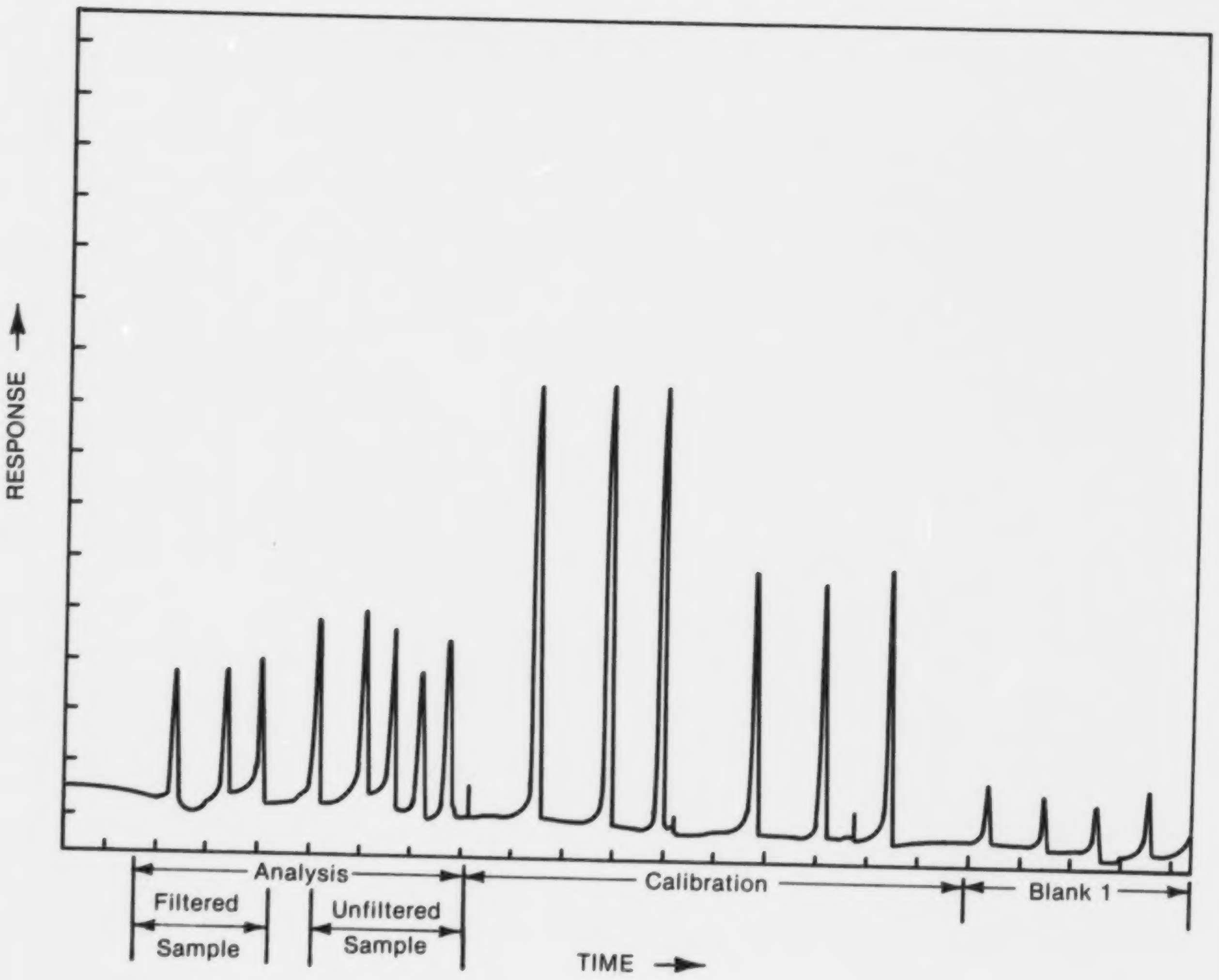

Figure B-5. Typical TOC analysis, performed August 9, 1978.

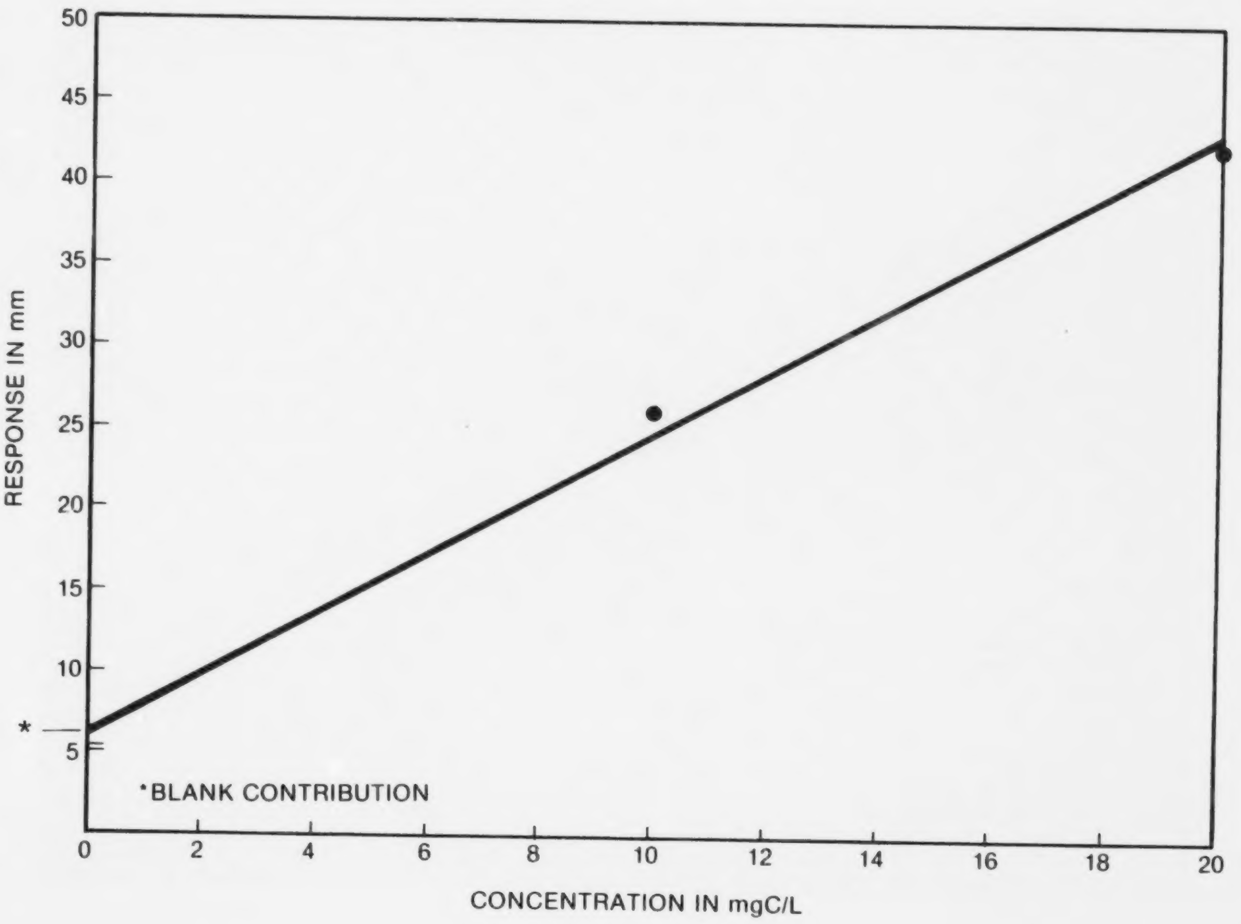

Figure B-6. Calibration of Beckman TOC Analyzer

* Blank contribution.

TABLE B-7. CALIBRATION DATA, BECKMAN TOC ANALYZER, AUGUST 9, 1978

Concentration (mgC/L)	Response in Peak Height (mm)	Average Response (mm)
0	5.0	
	5.2	5.3
	5.8	
10.05	27.4	
	25.0	25.9
	25.4	
20.10	41.5	
	43.1	42.3
	42.3	

samples is reproduced in Figure B-5. Calculations of results are reported in Table B-8. In this case, the dissolved nonvolatile fraction in the treated effluent was 4.2 mgC/L and suspended nonvolatile organic content corresponded to a difference between total nonvolatile organic fraction and dissolved nonvolatile organic fraction.

$$6.6 \text{ mgC/L} - 4.2 \text{ mgC/L} = 2.2 \text{ mgC/L}$$

Accuracy. Accuracy of the procedure for determining TOC in oily wastewaters was determined by adding known amounts of Prudhoe Bay crude to water, dispersing the oil with ultrasonic vibration, and then analyzing in a normal

TABLE B-8. TRIPLICATE ANALYSIS OF MILLIPORE-FILTERED AND ULTRASONATED UNFILTERED BALLAST WATER SAMPLES

	Response (mm)	Average Response (mm)	Average Response Less Blank	mgC/L
Millipore-Filtered	13.3			
Sample (Dissolved	12.6	13.2	7.9	4.2
Nonvolatile Fraction)	13.8			
Ultrasonated Unfiltered	17.2			
Sample (Total	18.0	17.7	12.4	6.6
Nonvolatile Fraction)	17.9			

manner. The results reported in Table B-9 indicate that the accuracy of the method is 99% with ±6% standard deviation.

Precision. The precision of the method was determined as reproducibility of multiple analyses of 10 samples of actual treated bilgewater. Three separate aqueous aliquots of the same sample were injected into the TOC analyzer. The results, shown in Table B-10, indicate a standard deviation of 2.4% for dissolved fraction and 2.1% for total nonvolatile fraction.

Instrument Performance Consistency. A record of calibration data was maintained for each day of field operations and a comparison was made of the daily variations in instrumental response. The calibration data generated during 10 days of the Summer 1978 study is reported as an example of instrument performance consistency in Table B-11. The reported data indicates that the Beckman TOC analyzer performed consistently without any drift in response.

Class Analysis, Dissolved Nonvolatile Organic Fraction

It was found by HPLC analysis that naphthalenes and phenols were present in dissolved nonvolatile fraction. Furthermore, it was established that no single separation technique can remove both types of compounds with equal efficiency. It was found by conducting recovery studies that while liquid-liquid extraction (using chloroform as a solvent) is effective in the removal of naphthalenic compounds from ballast water (80%+ recoveries are usually obtained), it was rather ineffective (less than 30% recovery) in the separation of highly polar phenolic compounds such as phenol, creosol, resorcinol, and hydroquinone. The column adsorption method of separation based on use of an Amberlite XAD-7 column was found to be highly effective in separating phenols from water (recoveries in the order of 75% are typically obtained), but was

TABLE B-9. ACCURACY OF MODIFIED TOC METHOD IN ANALYSIS OF PRUDHOE BAY CRUDE OIL

Oil in Water (mg/L)	mgC/L Present	mgC/L Found	% Recovery
21.4	18.4	19.7	107
38.5	33.1	32.5	98
54.9	47.2	43.8	93
78.2	67.3	62.0	92
113.0	97.1	93.7	97
3479.0	2950.0	3100.0	105
			99 ±6

TABLE B-10. REPRODUCIBILITY OF TOC ANALYSIS - DEVIATION FROM AVERAGE VALUE OF MULTIPLE ANALYSES IN TREATED BILGEWATER

% Dissolved Nonvolatile Fraction	% Deviation	% Total Nonvolatile Fraction	% Deviation
100.0	0	100.0	0
98.4	-1.6	94.2	-5.8
100.8	+0.8	101.6	+1.6
98.2	-1.8	98.0	-2.0
100.0	0	99.0	-1.0
102.7	+2.7	103.1	+3.1
96.0	-4.0	100.0	0
96.0	-4.0	95.0	-5.0
96.0	-4.0	101.9	+1.9
101.6	+1.6	103.7	+3.7
108.4	+8.4	99.4	-0.6
103.3	+3.3	101.2	+1.2
99.1	-0.9	98.2	-1.8
97.3	-2.7	95.1	-4.9
102.6	+2.6	106.1	+6.1
99.2	-0.8	96.7	-3.3
97.5	-2.5	100.8	+0.8
102.5	+2.5	103.3	+3.3
97.7	-2.3	103.3	+3.3
96.6	-3.4	100.0	0
105.7	+5.7	96.1	-3.9
100.0	0	102.2	+2.2
99.0	-0.9	99.3	-0.7
100.9	+0.9	97.8	-2.2
105.2	+5.2	94.7	-5.3
90.7	-9.3	106.1	+6.1
103.1	+3.1	98.5	-1.5
99.8	-5.2	95.1	-4.9
98.7	-1.3	101.0	+1.0
107.7	+7.7	102.9	+2.9
98.7	-1.3	108.3	+8.3
98.7	-1.3	97.8	-2.2
101.3	+1.3	95.3	-4.7
Relative Standard Deviation	±2.4		±2.1

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TABLE B-11. INSTRUMENT PERFORMANCE CONSISTENCY, TOC ANALYSIS

Date	Average Response Peak Height in mm 0 mgC/L Concentration	10 mgC/L Concentration	20 mgC/L Concentration
8-7-78	4.3	24.4	40.8
8-8-78	3.9	21.4	38.2
8-9-78	3.9	23.5	41.8
8-10-78	4.0	21.0	38.2
8-11-78	5.0	20.5	39.6
8-12-78	3.4	28.6	39.9
8-13-78	2.9	20.1	38.8
8-14-78	3.0	20.4	38.6
8-15-78	3.6	19.3	36.6
8-16-78	3.4	17.0	37.2
Average and Standard Deviation	3.7 ±0.6	21.6 ±3.2	39.0 ±1.6

found to be totally inefficient (less than 30% recoveries) in separating naphthalenic compounds. Because of this, two methods for separation of organic matter from water for detailed chemical analysis were used:

1. Liquid-liquid extraction with chloroform for analysis of naphthalenic compounds

2. Column separation on Amberlite XAD-7 for analysis of phenolic compounds

The class or group method of analysis as described in Appendix A was used for estimation of the concentration of phenolic and naphthalenic compounds in ballast water. High-pressure liquid chromatographic (HPLC) procedure was used.

The liquid-liquid extraction into chloroform and adsorption column separation on an Amberlite XAD-7 column followed by desorption into methanol were performed on-site in Valdez on the same day that samples were taken. The extracts were stored in a refrigerator and on completion of the Summer 1978 study they were shipped to California for analysis. The following quality control procedures were implemented.

Blanks. Blank determinations were performed on each day of analysis and compensation for blanks was made when needed.

Calibration. Calibration for phenolic compounds was carried out by preparing a mixture of hydroquinone, phenol, and creosol at 0.1-ppm concentration each and then carrying this mixture through a complete analysis, including adsorption on Amberlite XAD-7 column and desorption into methanol. Consequently, for these analyses the response factor was obtained by taking the recovery sample data (i.e., desorbed from XAD-7 column) for 0.1-ppm concentrations of hydroquinone, phenol, and creosol. The 0.1-ppm level was chosen over the 1.0-ppm because it was closer to the actual sample concentration.

Standard solutions of naphthalene, 1-methyl naphthalene, and a mixture of dimethyl naphthalenes were used for calibrating the HPLC for analysis of naphthalenic compounds.

Multipoint calibration (four points) was carried out for naphthalene and the measurements were made using the peak height method. The calibration graph for naphthalene is shown in Figure B-7.

Concentrations of naphthalene derivatives (methyl and dimethyl naphthalenes) were determined using the peak area measurement method. The instrumental response for 1-methyl naphthalene and dimethyl naphthalene was found to

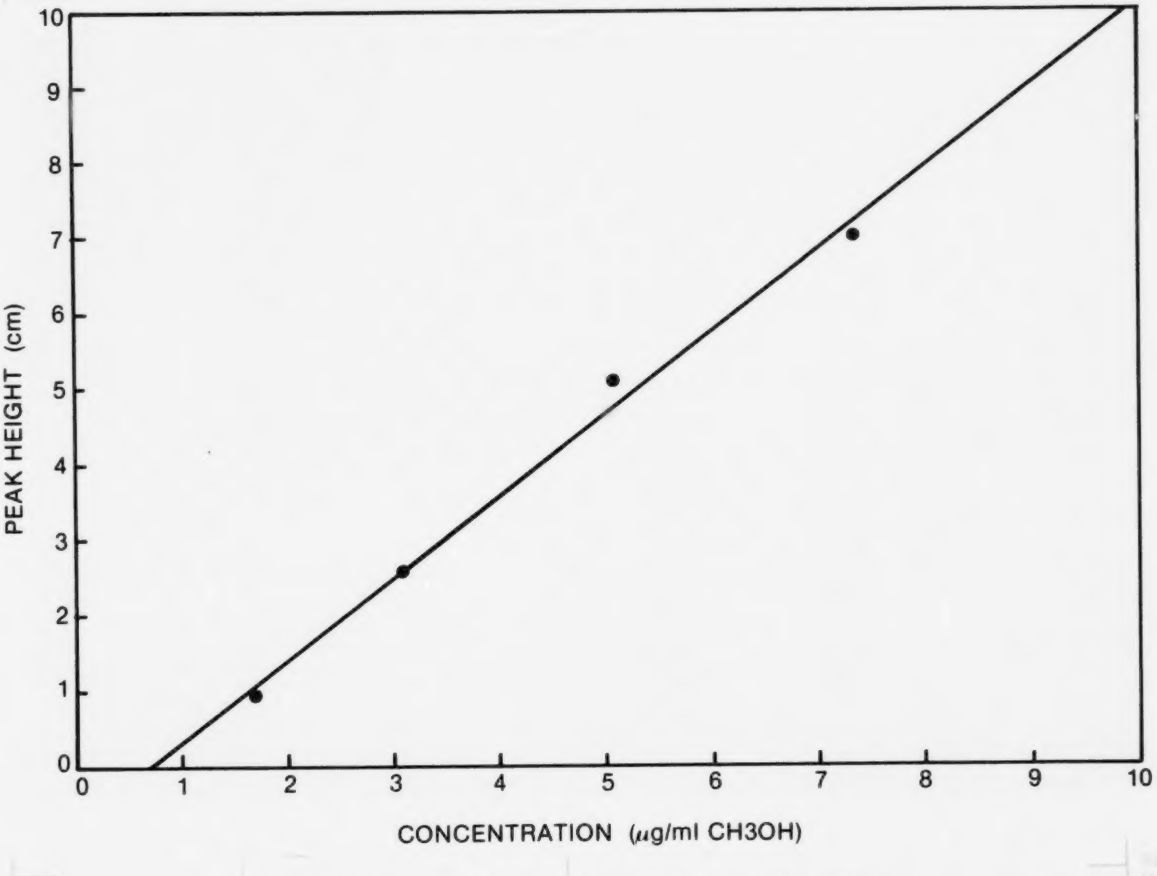

Figure B-7. Analytical curve for naphthalene.

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be very close (Table B-12) and an average value was used in calculating the results.

Replications. Eleven analyses were performed at least in duplicate and the average values were reported.

Accuracy. The accuracy of the method was determined by establishing recovery values for phenolic materials (hydroquinone, phenol, and creosol) and naphthalene. They are reported in Tables B-13 and B-14.

Standard Methods for Oil Analysis

Standard methods for oil analysis (Ref. B-4) were used for infrared (Method 502B) and gravimetric (Method 502A) determination of oil content in ballast waters. The analyses were carried out exactly as prescribed in the standard methods. The accuracy and precision of the standard methods used is reported in Ref. B-4.

Glassware Cleaning

Sampling bottles were washed with detergent, rinsed with distilled water, and dried in an oven prior to use. Contamination checks were carried out by introducing water blanks into containers, sparging, and conducting complete analyses for aromatic hydrocarbons.

QUALITY ASSURANCE

An independent quality assurance audit was carried out under the direction of Paul E. Mills, Quality Assurance Officer, IERL-Ci. Field audits were performed by C.L. Stratton and J.D. Bonds of Environmental Science and Engineering, Gainesville, Florida, under EPA Contract 68-03-2656. Audits were performed at the Rockwell International Environmental Monitoring & Services Center, Newbury Park, California, and in the Rockwell-operated laboratory in Valdez, Alaska, and on-site at the Alyeska Pipeline Service Company terminal treatment facility.

TABLE B-12. RESPONSE FACTOR OF 1-METHYL NAPHTHALENE AND ISOMERIC DIMETHYL NAPHTHALENES

Compound	Supplier	Area/ppm, Avg ±RSD	Number of Points
1-Methyl Naphthalene	Eastman, lot B8C	1.40 ±0.11	12
Dimethyl Naphthalene (mixture of isomers)	Aldrich, lot 092887	1.37 ±0.07	2

Note: The amount of naphthalene derivatives reported was calculated from the average response (1.39 area/ppm) of above compounds.

TABLE B-13. RECOVERIES OF PHENOLIC COMPOUNDS IN WATER SAMPLES BY AMBERLITE XAD-7 COLUMN SEPARATION METHOD

Compound	Concentration (ppm)	Peak Area (Int.Cts.)	Recovery Sample (Int. Cts.)	% Recovery
Hydroquinone	0.1	114,300	77,880	68
	1.0	543,100	268,950	50
Phenol	0.1	34,775	24,880	72
	1.0	350,250	252,150	72
Cresol	0.1	20,775	18,280	88
	1.0	197,600	180,300	91
Average Recovery				74%

TABLE B-14. RECOVERIES OF NAPHTHALENE IN WATER SAMPLE BY SOLVENT-SOLVENT EXTRACTION WITH CHLOROFORM

Sample No.	Concentration (ppm)	μg Spiked	μg Found Run 1	μg Found Run 2	μg Found Average	% Recovery
1	0.045	36	27.8	27.2	27.5	76.4
2	0.23	184	158	150	154	83.7
3	0.57	456	386	392	389	85.3
Average Recovery						82%

Newbury Park Quality Assurance Audit

The audit was preceded by a quality assurance pre-audit worksheet that was completed on May 31, 1979, and submitted to Environmental Sciences and Engineering, Inc., Gainesville, Florida. The pre-audit questionnaire addressed the following questions: project organization and technical qualifications of project team; project schedule; facilities and equipment conditions; analytical methodologies used in performance of this project; sampling and sample handling procedures; organization of field notebooks and worksheets; chain-of-custody procedures employed; type of samples collected and methods of preservation; specifics of quality control procedures including sample replication, spiking, data control and records.

The audit of Rockwell International, Newbury Park, California, was carried out on June 7, 1979, and involved the interview of the program manager, project officer, and technical personnel involved in the performance of the individual tasks under this program. Facilities used in program execution were inspected and the condition of instrumentation used was assessed. Personnel safety and instrument maintenance questions were addressed. Applicability of analytical procedures used was discussed in detail.

Discussions with Rockwell management and technical personnel were followed by examination of field sampling and analytical notebooks and original data files that are maintained by Rockwell as a record of raw data generated. The files related to all specific analytical operations were examined and random examples of raw data were selected for verification of reported data. Calculation of results was performed by auditors from the original recorded charts on gas chromatographs, HPLC, IR spectrometer and GC-MS.

Valdez Audit

The audit was performed on June 25, 1979, at the site of the Rockwell field laboratory in the State Court House, Valdez, Alaska, and on site at the Alyeska Pipeline Service Company terminal treatment facility. The daily cycle of field operations was monitored, including methods of sampling, sample preservation and documentation, laboratory receipt of samples, logging and recording, and actual performance of all analytical operations, including calculation and recording of the data. All personnel who performed field sampling and analytical work were interviewed as to the procedures used and technical competence.

A summary of the results of the audit follows.

QUALITY ASSURANCE AUDIT REPORT

Project: Characterization of a Ballast Water Treatment System
Contract/Grant No.: 68-03-2648 Project Officer: John Farlow
Laboratory Audited: Rockwell International
City: Newbury Park/Valdez State: California/Alaska
Laboratory Director: Dr. E. P. Parry

Audit Conducted by: Paul E. Mills*
Agency: IERL-Cincinnati
Date: 6/7/79 and 6/25/79

PURPOSE AND OBJECTIVES OF THE PROJECT:

The purpose of this project is to investigate the operation of a large, modern, on-shore oil-removal treatment system for oil tanker ballast water. This is a research and demonstration project, the data from which will be used to evaluate pollution control technology. The sampling and analysis program was not designed to provide data for purposes of regulation or compliance monitoring of the demonstration facility which was selected.

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* Field audit performed by C.L. Stratton and J.D. Bonds of Environmental Science and Engineering, Inc., Gainesville, Florida, under Contract No. 68-03-2656.

BRIEF DESCRIPTION OF THE SAMPLING AND ANALYTICAL REQUIREMENTS:

Sampling locations were selected at each point in the treatment process: (1) Raw wastewater from the ballast tanks of oil tankers, (2) Wastewater after treatment in a gravity separator, (3) water after treatment in dissolved air flotation chambers, and (4) the final effluent from the retention pond just before introduction into Valdez Harbor.

Initial analytical requirements for the project included gravimetric, IR, TOC, GC, GC/MS, and HPLC. The parameters determined included: Total oil in water by Freon extraction followed by gravimetric and IR; nonvolatile dissolved and nonvolatile suspended organics by TOC; volatile organics by GC with confirmation by GC/MS; and nonvolatile dissolved organics by chloroform extraction followed by HPLC and GC/MS. These methods were selected to provide a reasonably complete characterization of the wastewater at each sample point so that pollutant removal efficiencies can be determined.

RESULTS OF THE QUALITY ASSURANCE AUDIT

Organization and Personnel

The project team is small and closely supervised by the principal investigator, Mr. Ihor Lysyj. The project was well organized with respect to field sampling and analysis. Field personnel varied from trip to trip, with the exception of the principal investigator. However, the field personnel, on the June 25, 1979 visit, seemed adequately trained to perform their duties related to the field sampling and analysis effort.

Personnel at Rockwell's Newbury Park Laboratory were well trained and qualified to perform their project duties and exhibited a sound knowledge of their work.

Facilities

The facilities of the Alaskan Department of Environmental Regulation were used to set up the analytical equipment required to perform field analyses in Valdez. These facilities were found to be generally adequate. An exhaust hood and all necessary analytical instrumentation were transported by Rockwell to Valdez in good condition. The TOC analyzer had been modified from original specifications with different water traps, however, observations of operation indicated that the modifications had no deleterious effect on instrument capabilities. The other instrumentation used for the studies appeared to be in adequate condition to perform the required analyses.

RESULTS OF THE QUALITY ASSURANCE AUDIT
(continued)

Analytical Methodology

EPA methods were used for the TOC analysis. Non-standard research methods were used for the GC/MS and HPLC anlaysis. Two Standard Methods were used for the quantification of oil and grease: 502A (partition-gravimetric) and 502B (partition-IR). These methods were considered to be of limited value because of the loss of volatile species (benzene, toluene, and xylene) and consequently, poor representation of all oil residues present. Hence, project management chose to include an additional analysis in order to quantitate the volatile species. The purge and trap method that was chosen is well documented in a Rockwell procedure: "Aromatics in Oily Wastewaters." The documentation includes substantial accuracy and precision data. The method was also chosen because of its simplicity and ruggedness under reasonably remote field laboratory conditions. Analytical results seemed to agree well on one occasion with those analyzed by Radian Corporation for Alyeska Pipeline Co. The parameters measured and the analytical methods were selected to characterize the wastewater in sufficient detail in order to (1) determine effectiveness of petroleum removal, (2) identify chemical changes, and (3) establish final effluent quality. The selection of methods was, therefore, entirely justified.

Sampling and Sample Handling

Sample collection techniques were adequate and conscientiously observed. However, samples were not collected in replicate, even though it was stated in the Work Plan (p. 11) that six replicate samples should be collected at each point in order to achieve a 90% confidence level for the data. Upon at least one occasion (6/24/79) it was noted, in the field notebook, that two samples taken from a single point showed substantial visual differences. Field notebook entires were not signed by the collector or management personnel. There is some concern that volatile organics could be lost from the BTX fraction since a headspace was left in the sample containers. Samples were extracted immediately after collection (i.e., within one hour). Dye tracers were not used as indicated in the Work Plan (p. 5) to determine unit residence times. The sampling crew relied on Alyeska personnel to ascertain residence times based on flow measurements. Sample labeling was good.

Quality Control

Rockwell does not maintain an applicable laboratory quality assurance plan stating policy and procedures routinely applied to sampling and analysis. A project quality assurance plan (Section 6.4 of the Work Plan) was prepared and reviewed by the Project Officer. Although not stated in the project QA plan, most analyses were conducted in triplicate and the mean value reported after assessment of the analytical precision which generally appeared quite satisfactory. Spike recovery samples were run occasionally, the frequency could not be ascertained, but seemed generally adequate. In general, quality control documentation was sufficient and was readily accessible to the Principal Investigator.

RESULTS OF THE QUALITY ASSURANCE AUDIT
(continued)

Data Handling

All raw data is recorded in log books or on instrument recorder charts. Data calculations are performed in the laboratory in Newbury Park. The data files were examined and the following items were noted:

(1) Some recorder charts were not properly identified and could be irretrievably misplaced if removed for individual data folders.
(2) The file folders for each sample were well organized and complete.
(3) Check sample calculations were performed by the audit team on random raw data with results in agreement with the reported data.

In general, the data handling procedures are adequate.

QUALITY ASSURANCE DEFICIENCIES:

(1) Samples were not collected in replicate at each point as stated in the Work Plan, hence, sampling variability is not well established.
(2) Strip charts should be better identified and labeled.
(3) Departures from the Work Plan were not documented.
(4) A QA manual should be prepared by Rockwell, stating policies and procedures to maintain quality of sampling and analytical programs.
(5) The intensity of the sampling program is substantially less than stated in the Work Plan, because of restrictions on access to the site. For example, Table 6 of the Phase I Progress Report (12/1/78) compared final effluent data taken days before the gravity separator data. This was apparently unavoidable, but does detract from the substantiation of the study conclusions.

RECOMMENDED CORRECTIVE ACTIONS AND TIMETABLE:

Rockwell has good documentation of the analytical methods employed. This documentation should be incorporated into the final project report to substantiate these methods and to show the limitations of the standard total oil and grease methods in this case. Since there has been some question raised concerning the comparability of analytical methods used for the oil analysis, it may be of value to demonstrate the comparability (or lack of comparability) of the various methods by analysis of a crude oil reference sample which is available from EMSL-Ci.

Paul Mills	8/ 3/79
Signed	Date

QA Officer
Title

Distribution:

Project Officer
Quality Assurance Officer
Contractor/Grantee

CHAIN OF CUSTODY

All samples were collected by operating personnel and field analytical operations were performed the same day. Such samples remained under the control of Rockwell field teams from the time of sample collection to completion of the required analyses.

The samples that were required for determination of parameters which could not be performed in Valdez were pretreated on-site on the day during which they were collected. Pretreatment usually involved separation of organic matter from a water matrix by liquid-liquid extraction or macroreticular resin adsorption. The separated extracts were sealed and shipped by U.S. mail or by air freight to Rockwell EMSC in California. The condition of the shipping containers was examined upon receipt and from this point they remained in the custody of Rockwell personnel.

REFERENCES

B-1. Ballinger, D.G. Quality Assurance Update, Part II. Env. Sci. and Tech., 13, p. 1362, 11. 1979.

B-2. Costle, D. Memorandum, Quality Assurance Requirements for all EPA Extramural Projects Involving Environmental Measurement. June 14, 1979.

B-3. Sampling and Analysis Procedures of Screening of Industrial Effluent for Priority Pollutants. U.S. EPA Environmental Monitoring and Support Laboratory. Cincinnati, Ohio. April 1977.

B-4. American Public Health Association. Standard Methods for Examination of Water and Wastewater. 14th Edition. APHA, Washington, DC. 1975.

APPENDIX C

HISTORY OF PLANT OPERATION*

TREATMENT PLANT OPERATION

The ballast water treating facility at the Alyeska Pipeline Service Company Marine Terminal in Port Valdez, Alaska, began operation in August 1977. The plant was designed to remove oil from ballast water by the processes of gravity settling followed by dissolved air flotation. Ballast water enters one of three storage tanks where it is allowed to settle for a minimum of 4 hours. Settled ballast water containing small amounts of suspended and dissolved oil are drawn from the tank near the bottom. Oil floating on the surface of the ballast water is removed by a floating arm to a smaller storage tank.

When the plant began operation, an alum solution and a polyelectrolyte coagulant aid were injected into water drawn from the storage tanks. The process was designed to produce an alum floc in each of six flocculation chambers. Discharge from the flocculation chamber was via an underflow weir into a flotation basin. As the water passed through this weir, it was brought into contact with recycled ballast water into which air had been introduced under pressure. When the pressure was released as the recycle water was discharged from a header outside of the underflow weir, fine air bubbles were produced. These bubbles adhered to the floc formed in the wastewater, causing it to float. As the buoyant floc rose, it was to contact suspended oil particles in the wastewater and carry them to the surface. As the wastewater moved down the long flotation basins, surface skimmers removed the floating floc/oil sludge.

The clarified water overflows the flotation chambers into a single pH adjustment chamber. The pH of the water is monitored at the discharge of the pH adjustment chamber and caustic can be added to assure that effluent pH remains within permit limits. The treated water is then delivered into one of two impound basins.

Water from the impound basin is discharged to Port Valdez via a diffuser at an average depth of 70 meters approximately 366 meters from shore.

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* Abstracted from a letter from Frank Fisher, Alyeska Pipeline Service Company, to Bill Lamoreaux, U.S. EPA, Alaska Operations Office, dated May 8, 1979.

Shortly after the treatment plant started up, solids began forming in the impound basins inthe form of settleable solids, a floating scum and suspended solids. Plant personnel had to skim the surface of the basin with a vacuum truck daily and periodically draw down a basin and remove the settled solids with fire hoses. These solids were recycled back into the treatment process.

In late 1977 a program was initiated at the terminal to determine the cause of solids in the impound basins and to find a method of preventing their occurrence. Samples of effluent from the flotation chambers showed that floc formation was very poor and the floc observed was at best a finely divided microfloc. Efforts to produce a stronger floc that would form more rapidly were unsuccessful. A series of tests were conducted in which three pairs of flocculation and flotation chambers were isolated. Water passing through each pair of chambers was treated in a different manner. One pair of chambers was treated with alum and polyelectrolyte, a second pair was treated with a demulsifier and the third pair received no chemical treatment.

As a result of these tests, in late 1978 the use of alum and polyelectrolyte was stopped and the plant switched to using a demulsifier only. The use of this product has greatly reduced the solids inventory that was building up in the system.

In addition to the problem with post-flocculation in the impound basins, the treatment plant began receiving some ballast water containing hydrogen sulfide (H_2S) in late 1977. The source of this ballast water is discussed below in the section on shipping. The H_2S concerned Alyeska for two reasons. First, the gas was being stripped from the ballast water in the flotation chamber building, resulting in high concentrations of hydrogen sulfide in the building atmosphere. Alyeska's second concern was the possible effect the sulfate-reducing bacteria producing the gas might have on ballast water treatment. Data from other facilities and some initial problems at Valdez indicated that these bacteria can cause an oil/water emulsion that is extremely difficult to treat.

To eliminate the problem of hydrogen sulfide gas in the flotation building, Alyeska began a program of treating ballast containing hydrogen sulfide with hydrogen peroxide. The hydrogen peroxide rapidly oxidizes hydrogen sulfide to free sulfur and water. Soon after the problem was identified, terminal personnel built a temporary hydrogen peroxide injection system between the ballast water storage tanks and the DAF system. This temporary solution eliminated the problem of hydrogen sulfide gas in the flotation basin, but did not deal with the possible formation of the oil/water emulsion in the storage tanks. To prevent a buildup of sulfate-reducing bacteria in the storage tanks, a permanent hydrogen peroxide injection system was installed at the west manifold building of the terminal. This system treats ballast water from the ships prior to reaching the storage tanks.

SHIPPING ACTIVITY

Alyeska Pipeline Service Company is not privy to detailed information on the ships calling at Port Valdez. The company's port manual requires that the ship report the volume of ballast water on board, but not the point of origin of the ballast water. While the ship is required to report its last port-of-call, that may not be the source of the ballast water on board.

Some generalizations can be made about the source of ballast water. The majority of the crude oil shipped out of the terminal goes to four areas on the west coast: Puget Sound, San Francisco, Los Angeles, Long Beach, and Parita Bay, Panama.

Ballast water on ships out of Puget Sound, San Francisco, and Los Angeles/Long Beach would be primarily from these ports with some sea water added if additional heavy weather ballast was deemed necessary by the captain. Panama, however, presents a unique situation. In the past, crude oil carried to Panama was offloaded onto one of two mother ships anchored in Parita Bay. The crude was then transferred to smaller tankers capable of going through the Panama Canal to East Coast ports. Ballast water from these smaller tankers was transferred to the mother ships and from there to tankers returning to Port Valdez. Alyeska has no records of the original sources of ballast water from Panama.

The hydrogen sulfide problem at the treatment plant appeared only in ballast water from Panama. The long storage time for this ballast in transit from various East and Gulf Coast ports, and the warm temperatures in transit appeared to promote the growth of sulfate-reducing bacteria. In an attempt to inhibit the growth of these bacteria, a program of examining various methods of treatment was begun. At one point, a glutaraldehyde compound was tested on several ships out of Panama. This bactericide degrades rapidly once it is introduced into the ballast water. While the material appeared somewhat successful in the tests, it was extremely expensive and logistically difficult to use in the concentrations necessary to retard bacterial growth. A second test involved the use of hydrogen peroxide at Panama. Ballast water from the small tankers was treated with approximately 5 parts per million of hydrogen peroxide as it was delivered to the mother ship. The peroxide converted hydrogen sulfide to elemental sulfur and provided an oxygen source to bacteria in the water, thus preventing the anaerobic conditions necessary to promote the growth of sulfate-reducing bacteria. This treatment has continued to date with good results. To assure continued inhibition of hydrogen sulfide production, ballast pumped from the mother ships into the vessels returning to Valdez is treated with a second dose of hydrogen peroxide.

A marine terminal has recently been commissioned at Parita Bay, Panama. This terminal is designed to process all ballast water received from the East and Gulf Coast. As of May 9, 1979, Alyeska had been informed that the terminal was accepting ballast water from tankers and that one mother ship had been taken out of service and was sailing to Los Angeles. The second mother ship is to remain on station for 2 to 3 months to act as a backup to the terminal during its startup period. During this period she should be receiving very little if any ballast water from ships coming through the canal. When the terminal is operating smoothly, the second ship will leave. The Parita Bay terminal should eliminate the problem with hydrogen sulfide in Panamanian ballast, and possibly reduce the volume of ballast carried from the port. In the past, tankers returning to Valdez had to take on more contaminated ballast than they normally would carry. This was because of the lack of segregated ballast tanks on most of the smaller tankers sailing through the canal.

To the best of Alyeska's knowledge, no ships arriving at Port Valdez from ports other than Parita Bay are adding any chemicals to their ballast water. Normal ballasting operations throughout the world do not include any chemical treatment.

The estimated holding time for gallast en route to Port Valdez is approximately 15 days from Parita Bay, 8 days from Los Angeles, 7 days from San Francisco, and 5 days from Puget Sound. These times can vary by several days, depending on weather and fuel and/or maintenance needs.

CHEMICALS USED AT THE BALLAST TREATMENT PLANT

At present only two chemicals are being added to the ballast water at the treatment plant. These are hydrogen peroxide and an oil agglomerating chemical with the trade name of J-189 made by Tret-O-Lite Corp. The hydrogen peroxide is added at approximately 20 parts per million to all ballast water arriving from Panama. This is done to assure that any hydrogen sulfide that might be present in the ballast water will be oxidized to free sulfur. The J-189 is added approximately 5 parts per million to all ballast water entering the flotation chambers. This material causes the free oil remaining in the water to agglomerate and float to the surface of the flotation basins.

J-189 is a cationic, highly branched polyamine. Toxicity tests on Three-Spined Sticklebacks indicated a 96-hour LD50 of 32 parts per million. Little of this compound should be carried out with the discharge water. The majority will be bound with the agglomerate oil removed in the flotation chambers.

In addition to the hydrogen peroxide and J-189, the treatment plant carries an inventory of alum and caustic. Neither of these chemicals are being used at present and Alyeska has no plans to use them in the future. The plant also has storage capacity for a polyelectrolyte coagulant aid.

APPENDIX D

EXPERIMENTAL DATA*

INTRODUCTION

Field studies were carried out in Port Valdez, Alaska, to characterize the effectiveness of a modern, large-scale oily wastewater treatment plant in treating ballast water and producing a final effluent of acceptable quality. Performance characteristics of the principal treatment units (gravity separators and dissolved aeration-flotation separator) were evaluated. Their capabilities and limitations were investigated.

Three field studies were carried out: first summer study, August 1978; first winter study, February-March 1979; and second summer study, June-July 1979. During each study period a 10- to 11-day continium in time was scheduled to perform daily repetitive chemical analysis, and to correlate the resulting data with plant operating conditions.

During the first summer study the treatment plant was operated under conditions specified in the original plant design. Alum and polyelectrolyte aids were used in the dissolved aeration-flotation unit for oil-water separation. In late 1978 use of alum-polyelectrolyte was discontinued, and the plant switched to using a demulsifier (cationic, highly branched polyamine, J-189). Additionally, a practice of treating ballast with hydrogen peroxide was instituted. The Winter and Summer 1979 studies were carried out under modified plant operating conditions.

SUMMER 1978 STUDY

The first summer study was carried out August 7-18, 1978. During this period, chemical composition of the final effluent was characterized on 10 consecutive days (August 7-16) and the primary effluent from the gravity separator was characterized on two consecutive days (August 17-18). The estimated daily treatment process rates and water temperatures for this period are reported in Table D-1.

During this period the following tankers paid call at the terminal facility:

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* By Ihor Lysyj, Rockwell International, Newbury Park, California.

Date	Vessel
9 August 1978	T/V Overseas Juneau
11 August 1978	T/V Chevron California T/V Exxon San Francisco T/V Mobil Arctic
12 August 1978	T/V Brooks Range
13 August 1978	T/V Prince William Sound T/V Sohio Intrepid
16 August 1978	T/V Keystone Canyon
18 August 1978	T/V Maryland

TABLE D-1. ESTIMATED DAILY DISCHARGE RATES AND WATER TEMPERATURES, VALDEZ TERMINAL FACILITY, AUGUST 7-18, 1978

Date (1978)	Discharge Rate (thousands of cubic meters/day)	Water Temperature (°C)
8-7	32.6	17.8
8-8	15.5	17.8
8-9	36.0	15.6
8-10	31.0	17.8
8-11	70.0	17.8
8-12	78.7	16.8
8-13	62.1	--
8-14	41.3	17.2
8-15	21.6	17.8
8-16	65.9	16.7
8-17	65.5	16.7
8-18	44.7	16.1
Average	48.5	17.1

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The following analytical operations were performed daily in the Valdez laboratory:

Determination of volatile hydrocarbon content, including concentrations of benzene, toluene, xylenes/ethylbenzene, and estimation of concentration of aliphatic hydrocarbons based on n-hexane calibration.

Determination of nonvolatile, dissolved organic content.

Determination of suspended nonvolatile organic content.

Chloroform extraction for subsequent analysis of higher aromatics and polynuclear aromatic compounds.

Macroreticular column (Amberlite XAD-7) separation for subsequent determination of phenolic content.

Additionally, analyses for the oil were carried out daily using Standard Methods 502A and 502B. Those analyses were performed for comparative purposes.

The reduced data for the 10 days of testing the final effluent at the terminal facility in Port Valdez is shown in Table D-2.

The effluent from the gravity separator was examined on two consecutive days (August 17 and 18, 1978). The data is presented in Table D-3.

The comparison between chemical compositions of effluents from the gravity separator and the final treated discharge are shown in Table D-4. Examination of this table reveals that the TOL level in the gravity separator stream is approximately 20 mgC/L. This value is reduced by one-half by the secondary treatment, composed of aeration-flotation operations and reservoir holding. The secondary treatment not only reduces the total organic load of the process stream, but also produces significant changes in its chemical composition. The relative concentrations of volatile hydrocarbons is reduced from 61% to 48%, and aliphatic hydrocarbons (C_6 and lower) are totally eliminated by the secondary treatment. The concentration of aromatic hydrocarbons is reduced from 8.2 to 5.2 mgC/L, or by approximately 40%. The relative concentrations of dissolved nonvolatile organic fraction increased from 15% to 34%.

WINTER 1979 STUDY

The winter study was carried out during the February 19 through March 2 time period. The plant was operated at this time under modified conditions, using a demulsifer instead of alum-electrolyte in a dissolved air flotation-aeration unit of operation. During this work period an attempt was made to analyze each day samples of incoming ballast water from tankers; primary effluent from the gravity separator, and final treated effluent. The sampling sequence was initiated with the arrival of a tanker and subsequent sampling operations at the primary and final point of the process were programmed to correspond to the estimated time of arrival of the process water from a given tanker at a given process point. Process flowrates were used to estimate

TABLE D-2. CHEMICAL COMPOSITION OF FINAL EFFLUENT, VALDEZ, ALASKA BALLAST WATER TREATMENT PLANT, AUGUST 7-16, 1978

Date (1978):	8/7	8/8	8/9	8/10	8/11	8/12	8/13	8/14	8/15	8/16	Avg	%
Rate of Discharge (thousand cubic meters):	32.6	15.5	36.0	31.0	70.0	78.7	62.1	41.3	21.6	65.9		
Volatile Hydrocarbons						Concentration (mgC/L)						
Benzene	2.8	1.3	1.4	2.3	1.8	2.9	3.5	3.1	1.6	2.3	2.3	21
Toluene	1.9	1.3	1.3	1.9	1.5	2.5	2.1	2.5	1.7	2.0	1.9	18
Xylenes/Ethylbenzene	0.6	0.8	0.7	1.0	0.8	1.4	1.3	1.3	0.8	0.9	1.0	9
Other	0	0	0	0	0	0	0	0	0	0	0	0
Total	5.3	3.4	3.4	5.2	4.1	6.8	6.9	6.9	4.1	5.2	5.2	48
Nonvolatile Organics												
Dissolved	4.3	3.4	4.2	4.2	4.4	3.2	4.5	3.8	2.6	2.8	3.7	34
Suspended	3.3	0.9	2.4	3.0	0	3.5	1.7	2.0	1.6	0.4	1.9	18
Total	7.6	4.3	6.6	7.2	4.4	6.7	6.2	5.8	4.2	3.2	5.6	52
TOTAL ORGANIC LOAD*	12.9	7.7	10.0	12.4	8.5	13.5	13.1	12.7	8.3	8.4	10.8	

* Total Organic Load is a sum of volatile hydrocarbons converted to mgC/L value and dissolved and suspended organics also expressed in mgC/L.

TABLE D-3. CHEMICAL COMPOSITION OF EFFLUENT FROM GRAVITY SEPARATOR, VALDEZ BALLAST WATER TREATMENT PLANT, AUGUST 17-18, 1978

Date (1978):	8-17	8-18	Average	%
Rate of Discharge (thousand cubic meters):	65.5	44.7		
Volatile Hydrocarbons				
Benzene	2.9	4.3	3.6	18
Toluene	2.5	3.6	3.0	15
Xylenes/Ethylbenzene	1.4	1.8	1.6	8
Other	3.8	3.5	3.7	19
Total	10.6	13.2	11.9	61
Nonvolatile Organics				
Dissolved	1.9	4.0	3.0	15
Suspended	3.6	5.9	4.7	24
Total	5.5	9.9	7.7	39
TOTAL ORGANIC LOAD*	16.1	23.1	19.6	

* Total Organic Load is a sum of volatile hydrocarbons converted to mgC/L value and dissolved and suspended organics also expressed in mgC/L.

appropriate sampling times. This sampling scheme required seven-day-a-week, around-the-clock operation, and was carried out with the assistance of Alyeska personnel. On average, three sets of samples (incoming ballast, primary effluent from the gravity separator, and final treated effluent), were collected each day and analyzed for:

Volatile hydrocarbon content, including determination of aliphatic hydrocarbons (based on n-hexane calibration) and benzene, toluene, and xylenes plus ethylbenzene

Nonvolatile dissolved organic content

Suspended nonvolatile content

TABLE D-4. COMPARISON BETWEEN AVERAGE COMPOSITION IN EFFLUENTS FROM GRAVITY SEPARATOR AND FINAL EFFLUENT, AUGUST 17-18, 1978

	Concentration (mgC/L)	
	Gravity Separator	Final Effluent
Volatile Hydrocarbons		
Aliphatic	3.7	0
Aromatic	8.2	5.2
Benzene	3.6	2.3
Toluene	3.0	1.9
Xylenes/Ethylbenzene	1.6	1.0
Total Volatile Hydrocarbons	11.9	5.2
Nonvolatile Dissolved Organics	3.0	3.7
Suspended Organic Matter	4.7	1.9
TOTAL ORGANIC LOAD	19.6	10.8
Volatile Hydrocarbons		
Aliphatic	19%	0
Aromatic	41%	48%
Benzene	18%	21%
Toluene	15%	18%
Xylenes/Ethylbenzene	8%	9%
Total Volatile Hydrocarbons	61%	48%
Nonvolatile Dissolved Organics	15%	34%
Suspended Organic Matter	24%	18%

Total and percent values are calculated after normalization of all data in terms of mgC/L.

The treatment plant was operating near full capacity at this time, and the average volume of ballast water processed was almost twice that observed during the first summer study in August 1978. Table D-5 reports names and origin of tankers discharging at the terminal facility, and estimated daily rates of processed ballast water discharged .

TABLE D-5. PLANT OPERATIONS, FEBRUARY 19 - MARCH 2, 1979

Date (1979)	Vessel	Origin	Process Rate (thousand cubic meters)
2-19	T/V Southern Line	St. Croix	97.3
2-20	T/V Arco Heritage	Long Beach, California	98.4
2-21	T/V Exxon Philadelphia	San Francisco, California	94.6
2-22	T/V Overseas Natalie	Source of ballast Mississippi River	98.4
2-23	T/V Mobil Arctic	Ferndale, California	94.6
2-24	T/V Beaver State	Benicia, California	95.4
2-25	T/V Overseas Washington	Cherry Point, Washington	44.3
2-28	T/V Exxon New Orleans	San Francisco, California	95.8
3-1	T/V Exxon Baton Rouge	Benicia, California	96.9
Average			90.8

The temperatures of incoming ballast, effluent from the gravity separators, and the final effluent are reported in Table D-6.

Reduced data for the 10 days of testing of the final effluent is reported in Table D-7. Examination of this table reveals the data is similar to that generated during the Summer 1978 study. Unlike the summer study, however, aliphatic hydrocarbons were found in the final effluent. Lower process stream temperatures observed during the winter study might have contributed to less efficient removal of those compounds in the aeration-flotation basin.

The effluent from the gravity separator was examined during 10 days of plant operation, and the reduced data is shown in Table D-8. Examination of this data reveals that the average total organic load of the samples was approximately 16 mgC/L, somewhat lower than the value observed in the Summer 1978 study (approximately 20 mgC/L).

TABLE D-6. WATER TEMPERATURE OF PROCESS STREAM, FEBRUARY 19 - MARCH 2, 1979 (°C)

Date (1979)	Incoming Ballast	Primary Effluent	Final Effluent
2-19	6.0	9.0	10.0
2-20	4.0	6.0	8.0
2-21	7.2	7.5	10.0
2-22	9.5	7.8	11.0
2-23	6.0	8.0	10.0
2-24	9.0	-	10.0
2-26	4.0	7.2	7.0
2-28	7.2	9.5	9.5
3-1	-	10.0	9.0
3-2	-	6.7	8.0
Average	6.6	8.0	9.2

Difficulties were experienced in sampling of incoming ballast from arriving tankers. Because the chemical composition of ballast water in a tanker compartment varies in the vertical plane, representative sampling of incoming ballast water was rather difficult. No reliable scheme for representative sampling of the incoming ballast is available at this time, and the data on chemical composition of incoming ballast generally reflects poor reproducibility from sample to sample. Accordingly, the influent was characterized by a 10-day average chemical composition, as determined experimentally for dissolved and volatile fractions and an estimate of the concentration of suspended oil in the incoming ballast from plant operating data. This estimate is based on engineering process data: amount of oil recovered by the treatment plant and the volume of ballast processed.

For the month of February 1979, the average oil content in incoming ballast was calculated to be 7300 ppm and a sum of dissolved and volatile content averaged at 20 mgC/L.

The assessment of plant performance included determination of overall organic content reduction by the treatment processes and delineation of composition changes in the process stream as a result of various treatment operations. Documentation of day-to-day plant performance follows.

TABLE D-7. CHEMICAL COMPOSITION OF FINAL EFFLUENT, VALDEZ BALLAST WATER TREATMENT PLANT, FEBRUARY 19 - MARCH 2, 1979

Date (1979):	2-19	2-20	2-21	2-22	2-23	2-24	2-26	2-28	3-1	3-2	Avg	%
Rate of Discharge (thousand cubic meters):	97.3	98.4	94.6	98.4	94.6	95.4	44.3	95.8	96.9	94.6		
Volatile Hydrocarbons					Concentration (mgC/L)							
Benzene	2.9	1.4	2.0	2.7	1.9	2.2	1.2	1.7	1.4	1.3	1.9	17
Toluene	2.4	1.5	1.9	2.4	1.7	2.2	1.1	1.6	1.5	1.4	1.8	17
Xylenes/Ethylbenzene	1.1	0.9	1.0	0.9	0.8	0.9	0.5	0.8	0.8	0.9	0.9	8
Other	0.3	0.3	0.1	0.1	0.2	0.2	0.1	0.3	0.2	0.4	0.2	2
Total	6.7	4.1	5.0	6.1	4.6	5.5	2.9	4.4	3.9	4.0	4.8	44
Nonvolatile Organics												
Dissolved	5.8	4.7	5.7	5.0	5.4	5.4	4.6	4.5	4.7	5.7	5.2	48
Suspended	3.2	0	0	0.8	3.0	0.4	0.3	0	1.3	0	0.9	8
Total	9.0	4.7	5.7	5.8	8.4	5.8	4.9	4.5	6.0	5.7	6.1	56
TOTAL ORGANIC LOAD*	15.7	8.8	10.7	11.9	13.0	11.3	7.8	8.9	9.9	9.7	10.9	

* Total Organic Load is a sum of volatile hydrocarbons converted to mgC/L value and dissolved and suspended organics also expressed in mgC/L.

TABLE D-8. CHEMICAL COMPOSITION OF EFFLUENT FROM GRAVITY SEPARATOR, VALDEZ BALLAST WATER TREATMENT PLANT, FEBRUARY 19 - MARCH 2, 1979

Date (1979):	2-19	2-20	2-21	2-22	2-23	2-24	2-26	2-28	3-1	3-2	Avg	%
Rate of Discharge (thousand cubic meters)	97.3	98.4	94.6	98.4	94.6	95.4	44.3	95.8	96.9	94.6		
Volatile Hydrocarbons					Concentration (mgC/L)							
Benzene	3.2	1.4	2.5	3.5	3.5	3.0	2.5	1.7	2.1	2.4	2.6	16
Toluene	2.6	1.3	2.4	3.0	3.0	3.0	2.4	1.8	2.0	2.5	2.4	15
Xylenes/Ethylbenzene	1.2	0.8	1.3	1.3	1.3	1.4	1.3	1.1	1.1	1.7	1.3	8
Other	1.2	0.9	0.7	0.5	0.5	1.1	0.9	0.9	1.3	1.5	1.0	6
Total	8.2	4.4	6.9	8.3	8.3	8.5	7.1	5.5	6.5	8.1	7.3	45
Nonvolatile Organics												
Dissolved	3.8	3.2	4.2	5.7	5.0	5.6	5.5	6.7	6.1	8.0	5.4	34
Suspended	7.4	0.6	1.3	0.1	3.4	3.2	1.4	4.9	5.1	6.3	3.4	21
Total	11.2	3.8	5.5	5.8	8.4	8.8	6.9	11.6	11.2	14.3	8.8	55
TOTAL ORGANIC LOAD*	19.4	8.2	12.4	14.1	16.7	17.3	14.0	17.1	17.7	22.4	16.1	

* Total Organic Load is a sum of volatile hydrocarbons converted to mgC/L value and dissolved and suspended organics also expressed in mgC/L.

STUDY SEQUENCE NO. 1

Date: 2-19-79

Tanker, origin: Southern Line, St. Croix

Estimated plant discharge rate, thousands of cubic meters per day: 97.3 (Tank 94)

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	∿7320	
Primary separator effluent TOL value	19.4	99.7
Final effluent TOL value	15.7	99.8

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	9.1	7.4	1.7	19
Benzene, mg/L	3.5	3.2	0.3	9
Toluene, mg/L	2.9	2.6	0.3	10
Xylenes/Ethylbenzene, mg/L	1.3	1.2	0.1	8
Aliphatics, mg/L	1.4	0.4	1.0	71
Dissolved nonvolatile organics, mgC/L	3.8	5.8	+2.0	+52
Suspended nonvolatile organics, mgC/L	7.4	3.2	4.2	56

STUDY SEQUENCE NO. 2

Date: 2-20-79

Tanker, origin: Arco Heritage, Long Beach, California

Estimated plant discharge rate, thousands of cubic meters per day: 98.4 (Tank 94)

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	∿7320	
Primary separator effluent TOL value	8.2	99.9
Final effluent TOL value	8.8	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	4.7	4.4	0.3	6
Benzene, mg/L	1.3	1.5	-	-
Toluene, mg/L	1.4	1.6	-	-
Xylenes/Ethylbenzene, mg/L	0.9	1.0	-	-
Aliphatics, mg/L	1.1	0.3	0.7	63
Dissolved nonvolatile organics, mgC/L	3.2	4.7	-	-
Suspended nonvolatile organics, mgC/L	0.6	-	0.6	100

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STUDY SEQUENCE NO. 3

Date: 2-21-79

Tanker, origin: Exxon Philadelphia, San Francisco, California

Estimated plant discharge rate,
thousands of cubic meters per day: 94.6 (Tank 93)

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	12.4	99.8
Final effluent TOL value	10.7	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	7.6	5.5	2.1	27
Benzene, mg/L	2.8	2.2	0.6	21
Toluene, mg/L	2.6	2.1	0.5	19
Xylenes/Ethylbenzene, mg/L	1.4	1.1	0.3	21
Aliphatics, mg/L	0.8	0.1	0.7	88
Dissolved nonvolatile organics, mgC/L	4.2	5.7	-	-
Suspended nonvolatile organics, mgC/L	1.3	-	1.3	100

STUDY SEQUENCE NO. 4

Date: 2-22-79

Tanker, origin: Overseas Natalie, Mississippi River Source

Estimated plant discharge rate,
thousands of cubic meters per day: 98.4 (Tank 93)

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	14.0	99.8
Final effluent TOL value	11.9	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	9.1	6.7	2.4	26
Benzene, mg/L	3.8	3.0	0.8	21
Toluene, mg/L	3.3	2.6	0.7	21
Xylenes/Ethylbenzene, mg/L	1.4	1.0	0.4	28
Aliphatics, mg/L	0.6	0.1	0.5	83
Dissolved nonvolatile organics, mgC/L	5.7	5.0	0.7	12
Suspended nonvolatile organics, mgC/L	0.1	0.8	-	-

STUDY SEQUENCE NO. 5

Date: 2-23-79

Tanker, origin: Mobil Arctic, Ferndale, California

Estimated plant discharge rate,
thousands of cubic meters per day: 94.6 (Tank 93)

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	16.7	99.8
Final effluent TOL value	13.0	99.8

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	9.1	5.1	4.0	44
Benzene, mg/L	3.8	2.1	1.7	45
Toluene, mg/L	3.3	1.9	1.4	42
Xylenes/Ethylbenzene, mg/L	1.4	0.9	0.5	36
Aliphatics, mg/L	0.7	0.2	0.5	71
Dissolved nonvolatile organics, mgC/L	5.0	5.4	0.4	8
Suspended nonvolatile organics, mgC/L	3.4	3.0	0.4	12

STUDY SEQUENCE NO. 6

Date: 2-24-79

Tanker, origin: Beaver State, Benicia, California

Estimated plant discharge rate,
thousands of cubic meters per day: 95.4 (Tank 92)

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	∿7320	
Primary separator effluent TOL value	17.3	99.8
Final effluent TOL value	11.3	99.8

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	9.4	5.9	3.5	37
Benzene, mg/L	3.3	2.4	0.9	27
Toluene, mg/L	3.3	2.4	0.9	27
Xylenes/Ethylbenzene, mg/L	1.5	1.0	0.5	33
Aliphatics, mg/L	1.3	0.2	1.1	85
Dissolved nonvolatile organics, mgC/L	5.6	5.4	0.2	4
Suspended nonvolatile organics, mgC/L	3.2	0.4	2.8	88

STUDY SEQUENCE NO. 7

Date: 2-26-79

Tanker, origin: Overseas Washington, Cherry Point, Washington

Estimated plant discharge rate,
thousands of cubic meters per day: 44.3 (Tank 94)

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	14.0	99.8
Final effluent TOL value	7.8	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	7.0	3.2	3.8	54
Benzene, mg/L	2.7	1.3	1.4	52
Toluene, mg/L	2.6	1.2	1.4	54
Xylenes/Ethylbenzene, mg/L	1.4	0.6	0.8	57
Aliphatics, mg/L	1.0	0.1	0.9	90
Dissolved nonvolatile organics, mgC/L	5.5	4.6	0.9	16
Suspended nonvolatile organics, mgC/L	1.4	0.3	1.1	78

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STUDY SEQUENCE NO. 8

Date: 2-28-79

Tanker, origin: Exxon New Orleans, San Francisco, California

Estimated plant discharge rate,
thousands of cubic meters per day: 95.8

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	17.1	99.8
Final effluent TOL value	8.9	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	6.2	4.8	1.4	22.6
Benzene, mg/L	1.9	1.9	-	-
Toluene, mg/L	2.0	1.8	0.2	10
Xylenes/Ethylbenzene, mg/L	1.2	1.0	0.2	17
Aliphatics, mg/L	1.1	0.3	0.8	73
Dissolved nonvolatile organics, mgC/L	6.7	4.5	1.2	18
Suspended nonvolatile organics, mgC/L	4.9	-	4.9	100

STUDY SEQUENCE NO. 9

Date: 3-1-79

Tanker, origin: Exxon Baton Rouge, Benicia, California

Estimated plant discharge rate,
thousands of cubic meters per day: 96.9

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	17.7	99.8
Final effluent TOL value	9.9	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	7.2	4.3	2.9	40
Benzene, mg/L	2.3	1.5	0.8	35
Toluene, mg/L	2.2	1.7	0.5	23
Xylenes/Ethylbenzene, mg/L	1.2	0.9	0.3	25
Aliphatics, mg/L	1.5	0.2	1.3	87
Dissolved nonvolatile organics, mgC/L	6.1	4.7	1.4	23
Suspended nonvolatile organics, mgC/L	5.1	1.3	3.8	75

STUDY SEQUENCE NO. 10

Date: 3-2-79

Tanker, origin: American Sun, Richmond, California

Estimated plant discharge rate,
thousands of cubic meters per day: 94.6

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	22.4	99.7
Final effluent TOL value	9.7	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	9.1	4.4	4.7	52
Benzene, mg/L	2.6	1.4	1.2	46
Toluene, mg/L	2.8	1.5	1.3	46
Xylenes/Ethylbenzene, mg/L	1.9	1.0	0.9	47
Aliphatics, mg/L	1.8	0.5	1.3	72
Dissolved nonvolatile organics, mgC/L	8.0	5.7	2.3	29
Suspended nonvolatile organics, mgC/L	6.3	-	6.3	100

The summary of treatment plant performance in the Winter 1979 study is shown in Table D-9. Examination of this table reveals that the primary (gravity) separator performs the bulk of oil-water separation in the ballast water treatment plant. Approximately 99.8% of the organic matter is removed by this unit. The aeration-flotation secondary unit removes approximately 0.1% of the organic matter from the stream.

SUMMER 1979 STUDY

The second summer study was carried out during the June 19-30, 1979, time period. A demulsifier (polyamine J-189) was used as a chemical additive in the dissolved aeration treatment process. During this work period an attempt was made to analyze each day the primary effluent from the gravity separator, and the final treated effluent. Because of difficulties in representative sampling of incoming untreated ballast experienced during the Winter 1979

TABLE D-9. AVERAGE PLANT PERFORMANCE, VALDEZ BALLAST TREATMENT PLANT, MARCH 19 - APRIL 2, 1979

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~7320	
Primary separator effluent TOL value	16.1	99.8
Final effluent TOL value	10.9	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	7.9	5.2	2.7	34
Benzene, mg/L	2.8	2.0	0.8	29
Toluene, mg/L	2.6	2.0	0.6	23
Xylenes/Ethylbenzene, mg/L	1.4	1.0	0.4	28
Aliphatics, mg/L	1.1	0.2	0.9	82
Dissolved nonvolatile organics, mgC/L	5.4	5.2	0.2	4
Suspended nonvolatile organics, mgC/L	3.4	0.9	2.5	74

study, no attempt was made to sample incoming discharge from arriving tankers. Instead, the oil concentration in the incoming ballast was estimated from plant operating records. The sampling sequence was designed around process flowrates and arranged in such a way that the ballast of the same origin was sampled at the primary discharge from the gravity separator and the final discharge into the harbor.

On average, two sets of samples (primary effluent and final effluent) were collected each day and analyzed for:

Volatile hydrocarbon content, including determination of aliphatic hydrocarbons (based on n-hexane calibration) and benzene, toluene, and xylenes/ethylbenzene

Nonvolatile dissolved organic content

Suspended nonvolatile content

The discharge rate during this period fluctuated between 34.1 and 90.8 thousand cubic meters per day, averaging 49 thousand cubic meters per day. The rate fluctuation and average response during the June 1979 study were very similar to operating conditions experienced during the first summer study in August 1978. Table D-10 reports the names and origin of tankers discharging at the terminal facility, and estimated daily rates of processed ballast water discharged.

The temperature of primary and final effluent is reported in Table D-11.

Reduced data for the 11 days of testing of the final effluent is reported in Table D-12. Examination of this table reveals that the data is similar to that generated during the Summer 1978 and Winter 1979 studies.

The effluent from the gravity separator was examined during 11 days of testing and reduced data is shown in Table D-13. Examination of this table reveals a remarkable similarity to the chemical composition of the primary effluent as was observed during the Winter 1979 study. The average total organic load in the effluent from the primary (gravity) separator was 16.1 mgC/L in February 1979 and 16.1 mgC/L in the June 1979 study.

The assessment of plant performance included determination of overall organic content reduction by the treatment process and delineation of compositional changes in the process stream as a result of various treatment operations. Documentation of day-by-day plant performance follows. The summary is presented in Table D-14.

TABLE D-10. PORT ACTIVITY, JUNE 19-30, 1979

Date (1979)	Vessel	Origin	Process Rate (thousand cubic meters)
June 19	T/V Mobil Arctic	New Orleans, Louisiana	46.2
June 20	T/V Thompson Pass	San Francisco, California	60.9
	T/V Mobil Meridian	Ferndale, California	
June 21	T/V Atigun Pass	Panama	34.4
	T/V Glacier Bay	Los Angeles, California	
June 22	T/V Arco Anchorage	Long Beach, California	34.4
	T/V Sohio Resolute	Portland, Oregon	
June 24	T/V Chevron Mississippi	Cherry Point, Washington	55.3
	T/V Exxon North Slope	Benicia, California	
June 25	T/V Exxon Baton Rouge	San Francisco, California	23.1
June 26	T/V Keystone Canyon	St. Croix	85.5
	T/V Western Lion	St. Croix	
June 27	T/V Sinclair Texas	San Francisco, California	91.2
	T/V Western Lion	St. Croix	
June 28	T/V Mobil Meridian	Washington	57.2
	T/V Western Lion	St. Croix	
June 29	T/V Mobil Arctic	Cherry Point, Washington	34.4
	T/V Arco Fairbanks	Los Angeles, California	
June 30	T/V Mobil Arctic	Cherry Point, Washington	34.4
	T/V Arco Fairbanks	Los Angeles, California	
	T/V Exxon San Francisco	Long Beach, California	
	T/V Pt Alaska	Long Beach, California	
Average			49.2

TABLE D-11. WATER TEMPERATURE OF PROCESS STREAM, °C, JUNE 19-30, 1979

Date	Primary Effluent	Final Effluent
June 19	17.0	17.0
June 20	13.5	15.0
June 21	15.5	16.5
June 22	17.0	16.0
June 24	16.0	16.0
June 25	15.0	17.0
June 26	16.0	17.5
June 27	15.0	17.0
June 28	15.0	16.0
June 29	13.0	16.0
June 30	15.0	18.0
Average	15.3	16.5

TABLE D-12. CHEMICAL COMPOSITION OF FINAL EFFLUENT, VALDEZ BALLAST WATER TREATMENT PLANT, JUNE 19-30, 1979

Date (1979):	6/19	6/20	6/21	6/22	6/24	6/25	6/26	6/27	6/28	6/29	6/30	Avg	%
Rate of Discharge (thousand cubic meters):	46.2	60.9	34.4	34.4	55.3	23.1	85.5	91.2	57.2	34.4	34.4		
	Concentration (mgC/L)												
Volatile Hydrocarbons													
Benzene	1.4	2.4	2.5	1.4	2.7	0.4	1.6	2.1	1.9	1.9	1.5	1.8	18
Toluene	1.7	2.3	2.4	1.2	2.4	0.5	1.6	2.1	1.8	1.7	1.4	1.7	17
Xylenes/Ethylbenzene	0.9	0.7	0.8	0.4	0.9	0.6	0.7	1.1	0.7	0.7	0.6	0.7	7
Other	0.1	0.2	0.2	0.1	0.1	0.2	0.4	0.2	0.2	0.2	0.1	0.2	2
Total	4.1	5.6	5.9	3.1	6.1	1.7	4.3	5.5	4.6	4.5	3.6	4.4	44
Nonvolatile Organics													
Dissolved	2.4	-	-	5.6	5.3	3.6	3.9	3.8	3.2	3.0	-	3.9	38
Suspended	1.6	-	-	4.0	3.1	1.1	0.5	1.3	1.7	1.2	-	1.9	19
Total	4.0	-	-	9.6	8.4	4.7	4.4	5.1	4.9	4.2	-	5.8	57
TOTAL ORGANIC LOAD	8.1	-	-	12.7	14.5	6.4	8.7	10.6	9.5	8.7	-	10.2	

TABLE D-13. CHEMICAL COMPOSITION OF EFFLUENT FROM GRAVITY SEPARATOR, VALDEZ BALLAST WATER TREATMENT PLANT, JUNE 19-30, 1979

Date (1979)	6/19	6/20	6/21	6/22	6/24	6/25	6/26	6/27	6/28	6/29	6/30	Avg	%
Rate of Discharge (thousand cubic meters):	46.2	60.9	34.6	34.6	55.3	23.1	85.5	91.2	57.3	34.4	34.4		
Volatile Hydrocarbons						Concentration (mgC/L)							
Benzene	1.4	5.0	4.6	2.5	4.6	1.8	2.5	2.5	2.4	3.5	2.4	3.0	19
Toluene	1.8	4.9	4.3	2.3	4.5	2.2	2.4	2.6	2.4	3.1	2.2	3.0	19
Xylenes/Ethylbenzene	1.1	1.6	1.5	0.7	1.5	1.7	0.9	1.3	1.3	1.1	1.3	1.3	8
Other	1.1	1.5	1.8	1.1	2.2	1.7	1.5	1.8	1.5	2.1	0.9	1.6	10
Total	5.4	13.0	12.2	6.6	12.8	7.4	7.3	8.2	7.6	9.8	6.8	8.9	55
Nonvolatile Organics													
Dissolved	3.9	-	-	6.7	9.4	3.4	3.6	4.3	2.1	2.9	-	4.5	28
Suspended	3.0	-	-	0	1.1	7.0	3.2	3.1	2.2	1.9	-	2.7	17
Total	6.9	-	-	6.7	10.5	10.4	6.8	7.4	4.3	4.8	-	7.2	45
TOTAL ORGANIC LOAD	12.3	-	-	13.3	23.3	17.8	14.1	15.6	11.9	14.6	-	16.1	

STUDY SEQUENCE NO. 1

Date: 6-19-79

Tanker, origin: T/V Mobil Arctic, New Orleans, Louisiana

Estimated plant discharge rate,
thousands of cubic meters per day: 46.2

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	∿10,000	
Primary separator effluent TOL value	12.3	99.9
Final effluent TOL value	8.1	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	6.0	4.5	1.5	25
Benzene, mg/L	1.5	1.5	0	0
Toluene, mg/L	2.0	1.9	0.1	5
Xylenes/Ethylbenzene, mg/L	1.2	1.0	0.2	17
Aliphatics, mg/L	1.3	0.1	1.2	92
Dissolved nonvolatile organics, mgC/L	3.9	2.4	1.5	38
Suspended nonvolatile organics, mgC/L	3.0	1.6	1.4	47

STUDY SEQUENCE NO. 2

Date: 6-20-79

Tanker, origin: Thompson Pass, San Francisco, California
Mobil Meridian, Ferndale, California

Estimated plant discharge rate,
thousands of cubic meters per day: 60.9

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	∿10,000	
Primary separator effluent TOL value	NA*	-
Final effluent TOL value	NA*	-

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	14.4	6.1	8.3	58
Benzene, mg/L	5.5	2.6	2.9	53
Toluene, mg/L	5.4	2.5	2.9	54
Xylenes/Ethylbenzene, mg/L	1.8	0.8	1.0	56
Aliphatics, mg/L	1.7	0.2	1.5	88
Dissolved nonvolatile organics, mgC/L	-	-		
Suspended nonvolatile organics, mgC/L	-	-		

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* Analysis not completed.

STUDY SEQUENCE NO. 3

Date : 6-21-79

Tanker, origin: Atigun Pass, Panama
Glacier Bay, Los Angeles, California

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	NA*	
Final effluent TOL value	NA*	

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	13.4	6.5	6.9	51
Benzene, mg/L	5.0	2.8	2.2	44
Toluene, mg/L	4.7	2.6	2.1	45
Xylenes/Ethylbenzene, mg/L	1.6	0.9	0.7	44
Aliphatics, mg/L	2.1	0.2	1.9	90
Dissolved nonvolatile organics, mgC/L	-	-		
Suspended nonvolatile organics, mgC/L	-	-		

Analysis incomplete.

STUDY SEQUENCE NO. 4

Date: 6-22-69

Tanker, origin: Arco Anchorage, Long Beach, California
Sohio Resolute, Portland, Oregon

Estimated plant discharge rate,
thousands of cubic meters per day: 34.4

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	13.3	99.9
Final effluent TOL value	12.7	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	7.4	3.3	4.1	55
Benzene, mg/L	2.8	1.5	1.3	46
Toluene, mg/L	2.5	1.3	1.2	48
Xylenes/Ethylbenzene, mg/L	0.8	0.4	0.4	50
Aliphatics, mg/L	1.3	0.1	1.2	92
Dissolved nonvolatile organics, mgC/L	6.7	5.6	1.1	16
Suspended nonvolatile organics, mgC/L	-	4.0	-	-

STUDY SEQUENCE NO. 5

Date: 6-24-69

Tanker, origin: Chevron Mississippi, Cherry Point, Washington
Exxon North Slope, Benicia, California

Estimated plant discharge rate,
thousands of cubic meters per day: 55.3

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	23.5	99.8
Final effluent TOL value	14.5	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	14.3	6.9	7.4	52
Benzene, mg/L	5.1	3.0	2.1	41
Toluene, mg/L	4.9	2.6	2.3	47
Xylenes/Ethylbenzene, mg/L	1.7	1.0	0.7	41
Aliphatics, mg/L	2.6	0.3	2.3	88
Dissolved nonvolatile organics, mgC/L	9.4	5.3	4.1	44
Suspended nonvolatile organics, mgC/L	1.1	3.1	-	-

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STUDY SEQUENCE NO. 6

Date: 6-25-79

Tanker, origin: Exxon Baton Rouge, San Francisco, California

Estimated plant discharge rate,
thousands of cubic meters per day: 23.1

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	17.8	99.8
Final effluent TOL value	6.4	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	8.3	1.7	6.6	80
Benzene, mg/L	2.0	0.4	1.6	80
Toluene, mg/L	2.4	0.5	1.9	79
Xylenes/Ethylbenzene, mg/L	1.9	0.7	1.2	63
Aliphatics, mg/L	2.0	0.1	1.9	95
Dissolved nonvolatile organics, mgC/L	3.4	3.6	-	-
Suspended nonvolatile organics, mgC/L	7.0	1.1	5.9	84

STUDY SEQUENCE NO. 7

Date: 6-26-79

Tanker, origin: Keystone Canyon, Western Lion, St. Croix

Estimated plant discharge rate, thousands of cubic meters per day: 85.5

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	14.1	99.8
Final effluent TOL value	8.7	99.8

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	8.1	4.6	3.5	43
Benzene, mg/L	2.8	1.8	1.0	36
Toluene, mg/L	2.6	1.8	0.8	31
Xylenes/Ethylbenzene, mg/L	1.0	0.8	0.2	20
Aliphatics, mg/L	1.7	0.2	1.5	88
Dissolved nonvolatile organics, mgC/L	3.6	3.9	-	-
Suspended nonvolatile organics, mgC/L	3.2	0.5	2.7	84

STUDY SEQUENCE NO. 8

Date: 6-27-79

Tanker, origin: Sinclair Texas, San Francisco, California
Western Lion, St. Croix

Estimated plant discharge rate, thousands of cubic meters per day: 91.2

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	15.6	99.8
Final effluent TOL value	10.6	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	9.1	6.1	3.0	33
Benzene, mg/L	2.7	2.3	0.4	15
Toluene, mg/L	2.9	2.3	0.6	21
Xylenes/Ethylbenzene, mg/L	1.4	1.1	0.3	21
Aliphatics, mg/L	2.1	0.4	1.7	81
Dissolved nonvolatile organics, mgC/L	4.3	3.8	0.5	12
Suspended nonvolatile organics, mgC/L	3.1	1.3	1.8	58

STUDY SEQUENCE NO. 9

Date: 6-28-79

Tanker, origin: Mobil Meridian, Washington
Western Lion, St. Croix

Estimated plant discharge rate,
thousands of cubic meters per day: 57.2

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	11.9	99.9
Final effluent TOL value	9.5	99.9

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydorcarbons, mg/L	8.3	5.1	3.2	39
Benzene, mg/L	2.6	2.1	0.5	19
Toluene, mg/L	2.6	2.0	0.6	23
Xylenes/Ethylbenzene, mg/L	1.4	0.8	0.6	43
Aliphatics, mg/L	1.7	0.2	1.5	88
Dissolved nonvolatile organics, mgC/L	2.1	3.2	-	-
Suspended nonvolatile organics, mgC/L	2.1	1.7	0.4	19

STUDY SEQUENCE NO. 10

Date: 6-29-79

Tanker, origin: Mobil Arctic, Arco Fairbanks

Estimated plant discharge rate,
thousands of cubic meters per day: 34.4

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	14.6	99.8
Final effluent TOL value	8.7	99.1

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	10.9	5.0	5.9	54
Benzene, mg/L	3.9	2.1	1.8	46
Toluene, mg/L	3.4	1.9	1.5	44
Xylenes/Ethylbenzene, mg/L	1.2	0.8	0.4	33
Aliphatics, mg/L	2.4	0.2	2.2	92
Dissolved nonvolatile organics, mgC/L	2.9	3.0	-	-
Suspended nonvolatile organics, mgC/L	1.9	1.2	0.7	36

STUDY SEQUENCE NO. 11

Date: 6-30-79

Tanker, origin: Mobil Arctic, Cherry Point, Washington
Arco Fairbanks, Los Angeles, California

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	NA*	-
Final effluent TOL value	NA*	-

	Chemical Compositional Changes			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons, mg/L	7.5	4.0	3.5	47
Benzene, mg/L	2.6	1.7	0.9	35
Toluene, mg/L	2.4	1.5	0.9	38
Xylenes/Ethylbenzene, mg/L	1.4	0.7	0.7	50
Aliphatics, mg/L	1.1	0.1	1.0	91
Dissolved nonvolatile organics, mgC/L	-	-		
Suspended nonvolatile organics, mgC/L	-	-		

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* NA = analysis incomplete.

TABLE D-13. AVERAGE PLANT PERFORMANCE, VALDEZ BALLAST TREATMENT PLANT, JUNE 19-30, 1979

	Overall Organic Reduction	
	Concentration (ppm)	% Reduction
Incoming ballast estimated oil content	~10,000	
Primary separator effluent TOL value	16.1	99.8
Final effluent TOL value	10.2	99.9

	Chemical Compositional Changes (mgC/L)			
	Primary Effluent	Final Effluent	Differential	% Reduction
Volatile hydrocarbons				
Benzene	3.0	1.8	1.2	40
Toluene	3.0	1.7	1.3	43
Xylenes/Ethylbenzene	1.3	0.7	0.5	38
Aliphatics	1.6	0.2	1.4	88
Total	8.9	4.4	4.5	51
Dissolved nonvolatile organics	4.5	3.9	0.6	13
Suspended nonvolatile organics	2.7	1.8	0.9	33

APPENDIX E

CHEMICAL COMPOSITION OF DISSOLVED, NONVOLATILE FRACTIONS IN BALLAST WATER*

INTRODUCTION

Aromatic compounds, including hydrocarbons, are generally more water-soluble than aliphatic hydrocarbons. They are also believed to be more detrimental to aquatic life than aliphatic hydrocarbons because of higher toxicity. Crude and refined oils are known to contain the following aromatic compounds: aromatic and polynuclear aromatic hydrocarbons, phenols and cresols, heterocyclics (such as pyridine, quinoline), benzoic acid, esters and ethers. Many are quite water-soluble (Table E-1) and are expected to be found in the dissolved fraction of oily wastewaters.

Phenolic and naphthalenic compounds have been detected by HPLC in the treated effluent. Quantification and characterization of such compounds was undertaken in samples of process water collected during the first summer study (1978). Naphthalenic and phenolic compounds were analyzed in 10 samples of final effluent and 2 samples of effluent from the gravity separator.

It was established experimentally that different separation techniques were needed for separating phenols and for separation of naphthalenes from the water.

During the development of the analytical scheme for the characterization of oily wastewaters, liquid-liquid extraction methods as well as adsorption on macroreticular resins were studied. It was found that neither method alone is capable of satisfactory separation of petroleum-derived organic compounds from the water.

Naphthalene was effectively extracted and recovered into chloroform (average recovery 80%), but was poorly retained on Amberlite XAD-7 column. The phenols, especially the polyhydroxy type, were extracted rather poorly into chloroform (average recovery 30%), while being effectively separated and recovered from Amberlite XAD-7 resin column (average recovery 74%). For this reason, two separate separations were carried out: Amberlite XAD-7 column separation for analysis of phenolic compounds, and chloroform extraction for analysis of naphthalenic compounds. Stringent quality assurance procedures were applied to both techniques, and the analytical results were backed by recovery data.

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* By Ron Rushworth and Jack Cheng, Rockwell International, Newbury Park, California.

TABLE E-1. SOLUBILITY OF AROMATIC COMPOUNDS IN WATER (REF. E-1)

Compound	Concentration (mg/L)
Benzene	1780/20°C
Toluene	515/20°C
Xylenes	198/25°C
Naphthalene	30
Phenol	32,000/15°C
Resorcinol	2,290,000/30°C
Pyrrogallol	625,000/25°C
Cresol	28,000/30°C
Benzoic Acid	2,900
Pyridine	65,000/20°C
Quinoline	60,000

DETERMINATION OF PHENOLIC CONTENT

Twelve samples (10 discharge effluents and 2 gravity separator effluents) were analyzed for phenols using column adsorption concentration techniques followed by liquid chromatography. The column adsorption concentration and desorption step was performed on-site in Valdez, Alaska. The methanol eluates were sent to Rockwell International, Canoga Park, California, for liquid chromatographic analysis.

The incoming samples were received in 1-quart, wide-mouth glass bottles equipped with Teflon-lined caps. First, the volatile hydrocarbon content of the samples was determined using a nitrogen sparge-charcoal adsorption technique (Ref. E-2). A measured amount of acidified sample was then filtered through a Millipore Type AP, 40-microfiber glass depth prefilter, followed by a Millipore Type HA, 0.45-micron membrane filter using an all-glass vacuum filtration apparatus. The filters and apparatus were rinsed with 200 ml of distilled water prior to each use.

An adsorption column was used to separate and concentrate the organics from the seawater matrix. The procedure was similar to a method described by Junk, et al. (Ref. E-3). The apparatus consisted of a 1-liter-reservoir bulb connected to an 8.5-mm-ID x 140-mm glass column filled with approximately 8 ml of Amberlite XAD-7 resin. The resin was pretreated by slurrying in methanol and decanting off the fines. The resin was then Soxhlet-extracted for 8 hours each with diethyl ether, acetonitrole, and methanol. The purified resin was introduced as a slurry into the glass column and stored under methanol. The column was repacked (using the same resin) after each run because of resin shrinkage and subsequent channeling. Approximately 50 to 100 ml of methanol was used to rinse the column after repacking. Prior to analysis, the column was rinsed with 200 ml of distilled water to remove the methanol and condition the column. The acidified and filtered sample was passed through the above-described column at a flowrate of approximately 8 ml/minute. The retained organics were then desorbed with 25 ml of methanol. The eluates were collected in 25-ml glass bottles for shipment to Rockwell International, Canoga Park, California.

After the eluates were received at Canoga Park, the volumes were reduced from 25 ml to 10 ml by flowing a gentle stream of nitrogen over the surface of the methanol. Aliquots were then taken from the 10-ml volume for liquid chromatographic analysis. The analysis was carried out under the following conditions:

Instrument:	Spectra Physics Model 3500 B HPLC
Detector:	Spectra Physics Model SP8200, 254 nm wavelength
Column:	Whatman Partisil-10 ODS-2, 25 cm x 4.6 mm 1 or 2 column as stated in text
Mobile Phase:	70% methanol, 30% water by volume
Flowrates:	Stated in text
Sample Size:	10 microliters
Integrator:	Hewlett-Packard Model 3370A
Recorder Speed:	1 cm/minute

Initially, a single Whatman Partisil PXS 10/25 ODS-2 column was used (Ref. E-2). A large solvent peak precluded effective resolution of phenolic compounds from the solvent peak.

To help alleviate the integration problem, a second Whatman column (identical to the first) was added in series to increase the resolution so that the large peak and disruption could be integrated out. It was found that by using two columns, a semi-quantitative estimate of peak areas could be obtained. The following retention times were obtained using the two-column system and a flowrate of 0.84 ml/minute:

Compound	Retention Time (Minutes)
Resorcinol	6.5
Pyrogallol	6.7
Hydroquinone	7.9

Compound	Retention Time (Minutes)
Phenol	9.0
Cresol	10.8
Pyridine	13.4
Benzene	17.3
Quinoline	18.8
Toluene	25.3
Xylenes	36.5

Note: The above compounds were dissolved in methanol and injected using a fixed-volume injection loop. The retention time windows for the "class separations" were adjusted to reflect the longer retention times.

SAMPLE ANALYSIS

In the sample chromatograms, no significant peaks were found to elute prior to the large unidentified "solvent-type" peaks at 6 minutes. The origin of this peak has not been established, but it is present in all eluates -- blanks, controls, as well as samples. Therefore, integration was started at approximately 6.2 minutes by tangent skimming the tail of this large peak. It was noted that the retention time for pyridine shifted as the column became acidic. Using neutral solutions, the retention time for pyridine was 13.5 minutes, after putting through a number of acidic samples (the Alyeska samples are acidic due to the initial HCl acidification), the retention time for pyridine shifted to 20.8 minutes. Quinoline exhibited similar shifts in retention time. In view of this and the fact that all volatile aromatic hydrocarbons were removed from the sample during the sparging step, the phenolic retention time window was extended to approximately 20 minutes.

SAMPLE QUANTIFICATION

The sample chromatograms were integrated from 6.2 minutes to approximately 20 minutes to obtain a rough estimate of the levels of compounds eluting within the retention time window for phenolics. The individual peak areas were added and the sum multiplied by the phenolic class response factor. The class response factor was obtained using the method of Lysyj (Ref. E-2) where he obtained class factors for each class (i.e., phenolics, alkyl benzenes, etc.) of interest by averaging the individual responses of each compound (same concentration) in its class. He states that "while absorption characteristics of different aromatic compounds vary, there is a similarity in the intensity of responses within each of the specified groupings: phenolic compounds, alkylbenzenes, nitrogen heterocyclics, etc. Because of this it is possible to establish an average UV response factor for each class of interest."

For these analyses, the response factor was obtained by taking the recovery sample data (i.e., desorbed from XAD-7 column) for 0.1-ppm concentrations of hydroquinone, phenol, and cresol. The 0.1-ppm level was chosen over the 1.0 ppm because it was closer to the sample concentration. The calculations are as follows:

$$\text{Response Factor} = \frac{\text{ppm}}{\text{Int.Cts}} = \frac{0.1\ \text{ppm hydroquinone} + 0.1\ \text{ppm phenol} + 0.1\ \text{ppm cresol}}{77{,}880 + 24{,}880 + 18{,}280}$$

$$= 2.48 \times 10^{-6}\ \text{ppm/Int. Ct.}$$

Table E-2 summarizes the sample results.

DETERMINATION OF NAPHTHALENIC CONTENT

Twelve samples (10 discharge effluents and 2 gravity separator effluents) were analyzed for naphthalenic compounds using the chloroform extraction technique followed by liquid chromatography. The chloroform extraction step was performed on-site in Valdez, Alaska. The chloroform extracts were sent to Rockwell International, Newbury Park, California, for liquid chromatographic analysis.

The incoming samples were received in 1-quart, wide-mouthed glass bottles equipped with Teflon-lined caps. After the volatile organic content of the samples was separated by sparging for the analysis of volatiles, the measured volume of sample was acidified and filtered through a Millipore Type AP 40-microfiberglass depth prefilter, followed by a Millipore Type HA 0.45-micron filter using an all-glass vacuum filtration apparatus. The filters and apparatus were rinsed with 200 ml of distilled water prior to each use.

The filtered water sample was extracted into three successive 50-ml volumes of chloroform. The extracts were combined and 5 ml of ethanol was added to the combined extract. The volume of extract was reduced to 5 ml in a Kuderna-Danish evaporator. Because of the lower boiling point of chloroform, the residual liquid was composed essentially of ethanol. The addition of ethanol was found to be necessary to overcome phase separation (chloroform-water). Such separations were experienced when the extract containing chloroform and residual water was reduced to a small volume.

Aliquots were taken from 5 ml volume for liquid chromatographic analysis. The analysis was carried out under the following conditions:

Instrument:	Altex HPLC Model 100
Detector:	UV 254 nm at 0.04 AUFS
Column:	3.5 x 250 mm Lichrosorb, C-18
Mobile Phase:	70:30 v/v methanol: water flowrate 1.0 ml/minute
Sample Size:	50 microliters

SAMPLE QUANTIFICATION

The four-point calibration curve for naphthalene is based on peak height measurement, and was used for calculation of naphthalene concentration. Both methyl and dimethyl derivatives of naphthalene were found in ballast waters. Since peaks for those derivatives overlap, a common response factor based on peak area was developed.

TABLE E-2. PHENOLIC CONTENT OF PROCESS WATER

Sample Date	Sum of Peak Areas (Int.Cts)	Response Factor (ppm/Int.Ct)	ppm (not corrected for volume)	Sample Volume (L)	ppm (corrected for volume)
Filtered Samples, Final Effluent					
8-7-78	125,669	2.48×10^{-6}	0.31	0.70	0.4
8-8-78	162,094		0.40	0.75	0.5
8-9-78	155,024		0.38	0.75	0.5
8-10-78	259,839		0.64	0.84	0.8
8-11-78	153,711		0.38	0.85	0.4
8-12-78	149,798		0.37	0.85	0.4
8-13-78	263,092		0.65	0.84	0.8
8-14-78	327,477		0.81	0.84	1.0
8-15-78	191,011		0.47	0.82	0.6
8-16-78	231,813		0.57	0.83	0.7
Average					0.6
Unfiltered Samples, Final Effluent					
8-13-79	247,354		0.61	0.85	0.7
8-14-79	173,110		0.43	0.84	0.5
8-15-79	236,139		0.59	0.84	0.7
8-16-79	253,506		0.63	0.83	0.8
Average					0.7
Filtered Samples, Gravity Separator Effluent					
8-17-79	74,046		0.18	0.84	0.2
8-18-79	171,648		0.43	0.83	0.5
Average					0.4
Unfiltered Samples, Gravity Separator Effluent					
8-17-79	218,295		0.54	0.84	0.6
8-18-79	216,250	2.48×10^{-6}	0.54	0.75	0.7
Average					0.7

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The response factors for naphthalene derivatives are as follows:

	Area/ppm
1-methyl naphthalene	1.40 ±0.11
dimethyl naphthalene isomers	1.37 ±0.07

The amount of naphthalene derivatives reported here is calculated on the basis of an average response factor (1.39 area/ppm). The results are summarized in Table E-3.

The summary of chemical data for phenolic and naphthalenic compounds is presented in Table E-4. It was found that concentrations of phenolic compounds fluctuated in the primary and final effluent between 0.4 and 1 ppm, while naphthalenic compounds fluctuated between 0.24 and 0.35 ppm. Observed fluctuations appeared to be independent of flowrates, and the average concentrations

TABLE E-3. NAPHTHALENIC CONTENT OF PROCESSED WATER

Sample Date	Naphthalene (ppm)			Naphthalene Derivatives (ppm)		
	Run 1	Run 2	Average	Run 1	Run 2	Average
			Final Effluent			
8-7-78	0.078	0.079	0.079	0.261	0.262	0.262
8-8-78	0.034	0.035	0.035	0.197	0.164	0.181
8-9-78	0.052	0.052	0.052	0.221	0.187	0.204
8-10-78	0.065	0.065	0.065	0.238	0.244	0.241
8-11-78	0.040	0.042	0.041	0.154	0.165	0.160
8-12-78	0.080	0.079	0.080	0.219	0.227	0.223
8-13-78	0.046	0.046	0.046	0.152	0.167	0.160
8-14-78	0.051	0.050	0.051	0.168	-	0.168
8-15-78	0.087	0.087	0.087	0.201	-	0.201
8-16-78	0.067	0.067	0.067	0.196	0.265	0.231
Average			0.060			0.203
			Effluent From Gravity Separator			
8-17-78	0.081	0.082	0.082	0.281	0.205	0.243
8-18-78	0.028	0.028	0.028	0.081	0.100	0.091
Average			0.055			0.167

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TABLE E-4. DISSOLVED ORGANIC FRACTION, TERMINAL TREATMENT FACILITY, PORT VALDEZ, ALASKA, SUMMER 1978 STUDY

	Final Effluent											Primary Effluent		
Date, 1978:	8/7	8/8	8/9	8/10	8/11	8/12	8/13	8/14	8/15	8/16	Avg	8/17	8/18	Avg
Daily Discharge (thousand cubic meters)	32.6	15.5	36.0	31.0	70.0	78.7	62.1	41.3	21.6	65.9	45.4			
Dissolved Nonvolatile Organics (mgC/L)	4.3	3.4	4.2	4.2	4.4	3.2	4.5	3.8	2.6	2.8	3.7	1.9	4.0	3.0
Phenolic Compounds (mg/L)	0.4	0.5	0.5	0.8	0.4	0.4	0.8	1.0	0.6	0.7	0.6	0.2	0.5	0.4
Naphthalenic Compounds (mg/L)	0.341	0.216	0.256	0.276	0.201	0.303	0.206	0.219	0.288	0.298	0.26	0.325	0.119	0.23
Naphthalene (mg/L)	0.079	0.035	0.052	0.065	0.041	0.080	0.046	0.051	0.087	0.067	0.06	0.082	0.028	0.06
Naphthalene Derivatives (mg/L)	0.262	0.181	0.204	0.248	0.160	0.223	0.160	0.168	0.201	0.231	0.20	0.243	0.091	0.17

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in the primary and final effluent were within the experimental error. It must be concluded that secondary treatment did not produce observable effects on concentrations of phenolic and naphthalenic compounds.

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E-1. Verschyesseh, K. Handbook of Environmental Data on Organic Chemicals. Van Nostrand-Reinhold Co., New York. 1977.

E-2. Lysyj, I., and E.C. Russell. Determination of Aromatic and PAH Content of Oily Wastewaters. Symposium on Analytical Chemistry of Petroleum Hydrocarbons in the Marine/Aquatic Environment. Vol. 23, No. 3. American Chemical Society. Washington, DC. August 1978.

E-3. Junk, G.A., et al. Resin Sorption Method for Monitoring Selected Contaminants in Water. Identification and Analysis of Pollutants in Water. Ann Arbor Science Publishers, Inc. Ann Arbor, Michigan. 1976.

APPENDIX F

COMPARATIVE EVALUATION OF STANDARD AND MODIFIED METHODS FOR TOTAL OIL DETERMINATION*

INTRODUCTION

It was discovered early in this program that standard methods for analysis of oil and grease, based either on a gravimetric procedure (Standard Method 502A, Ref. F-1) or on IR determination (Standard Method 502B) do not accurately reflect the organic load in the process stream of the ballast treatment plant or in treated effluent discharged into Valdez Harbor. At the request of the EPA Project Officer, a comparative evaluation of standard and modified methods for total oil determination was carried out.

Under this subtask of the program, various methods for calibrating the IR procedure were examined and the comparative effectiveness of Freon 113 and carbon tetrachloride extraction methods was studied. Recovery data was assembled for synthetic mixtures of Prudhoe Bay crude oil in water and for treated ballast effluent. The extraction of treated effluent samples into Freon 113 and carbon tetrachloride were performed in Valdez, Alaska, and the extracts were shipped to California for analysis.

EXPERIMENTAL

1. Instrumentation. A Perkin-Elmer Model 283 double-beam optical null filter-grating infrared spectrophotometer was used for all quantitative infrared measurements. The spectrometer was operated in the linear absorbance mode. A Hewlett-Packard Model 3371B electronic integrator was connected to the external readout of the spectrometer to obtain area measurements.

2. Samples. The incoming extracts were received in 100-ml glass bottles equipped with aluminum foil-lined caps. The samples were kept refrigerated until analyzed.

3. Analytical Procedures. Standard procedures for infrared and gravimetric determination of grease and oil, Methods 502A and 502B as described in Standard Methods for Examination of Water and Wastewater, Ref. F-1, were closely followed.

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* By R. Rushworth, Rockwell International, Canoga Park, California.

4. Oil for Infrared Calibration

    a. Prudhoe Bay crude oil (PBC) supplied by Ihor Lysyj of EMSC

    b. Vacuum stripped Prudhoe Bay crude oil (VSPBC) prepared by placing 5 grams of PBC in a 250-ml round-bottom flask, stirring with a magnetic stir bar and vacuum stripping at less than 1 tor for 30 minutes

    c. Reference oil (RO) - 37.5% isooctane, 37.5% hexadecane, 25% benzene as stated in Ref. F-1

5. Extraction Solvents

    a. Freon 113 (1,1,2-trichloro -1,2,2-trifluoroethane)

    b. Carbon tetrachloride (CCl_4)

Calibration

Standard solutions of Prudhoe Bay crude oil (PBC), vacuum-stripped Prudhoe Bay crude oil (VSPBC), and synthetic reference oil (RO) were prepared in 0 to 200 mg/L concentration range. One set of standard solutions was prepared in Freon 113, the other in carbon tetrachloride.

Calibration curves in IR absorbance for Freon solutions indicate only minor differences in slopes between Prudhoe Bay crude oil standard, vacuum-stripped Prudhoe Bay crude oil standard, and reference oil mixture.

Calibration curves in IR absorbance for carbon tetrachloride solution reveal that the slopes for Prudhoe Bay crude oil standard and vacuum-distilled Prudhoe Bay crude oil are essentially the same. The reference oil curve follows the slope of two others in the 0 to 100 mg/L concentration range, but deflect somehow at higher concentration levels.

Comparison of absorption curves of various standards in Freon 113 and carbon tetrachloride suggests that each of the standards prepared in carbon tetrachloride adsorbed IR radiation more intensely than the same standard prepared in Freon 113.

Prudhoe Bay Crude Oil Recovery

Triplicate extractions of known amounts of oil-in-water dispersions at two difference concentrations were made using Freon and CCl_4.

Deionized water (900 ml) was added to clean 1000-ml separatory funnels fitted with Teflon stopcocks. Quantities (5 mg and 20 mg) of oil were weighed by difference from a micro syringe into the separatory funnels. The stoppered funnels were then agitated vigorously to disperse the oil as completely as possible. Each water dispersion was then acidified with 1:1 HCl to pH less than 2 (4.5 ml) and agitated again vigorously. Each dispersion was then extracted by adding 30 ml of solvent, shaking vigorously for 2 minutes and the

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phases allowed to separate. The solvent layer was removed and filtered through solvent-washed Whatman 1PS phase separation filter paper into a clean 100-ml volumetric flask. The water phase was extracted two additional times with 30-ml aliquots of the solvent, and the solvent filtered and collected in the same 100-ml volumetric flask. The funnel and filter were rinsed with an additional few ml of solvent and the washings added to the flask. The flask was then made to volume with solvent. The results are presented in Table F-1. This table reveals that when using Freon as the extraction solvent, the average recoveries (PBC, VSPBC, and RO) at the 5-mg and 20-mg concentrations were 84.7% and 89.2%. For carbon tetrachloride, the average recoveries at 5 mg and 20 mg levels were 73.6% and 90.4%. Thus, Freon results in a 10% higher recovery of PBC at the 5-mg concentration and is as good as CCl_4 at the higher level.

Infrared Analysis of Alyeska BWT Effluent Extracts

Six replicate samples of effluent were taken on each of the two sampling days. Each day, three samples were extracted with Freon and three with carbon tetrachloride. The total organic load of the collected samples was determined by the procedure described in Appendix A. The total organic load (TOL) of samples collected on August 3, 1979, was 5.8 mgC/L, and volatile hydrocarbons constituted only 0.8 mgC/L. The samples collected on August 6, 1979, contained 14.5 mgC/L and volatile hydrocarbons were at a 4.3-mgC/L concentration level. The extractions were performed on the day of sampling in Valdez, Alaska, and the extracts were air shipped to California for analysis.

Prior to analysis, the sample extracts were quantitatively transferred to 100-ml volumetric flasks and made to volume with the respective solvent. A pair of matched 1-cm-path-length quartz cells were used for the absorbance measurements. Neat solvent was used in the reference cell. The samples and standards were scanned from 3200 cm^{-1} to 2700 cm^{-1} at a rate of 100 cm^{-1}/min. The infrared absorbance of the samples and standards was measured by constructing a straight baseline over the range of the scan and measuring the absorbance of the peak maximum and subtracting the baseline absorbance at that point. Area integration was started at the beginning (3200 cm^{-1}) and stopped at the end (2700 cm^{-1}) of each scan. Each sample and standard was scanned twice and the average value reported. After the infrared absorbance and area values were obtained, the Prudhoe Bay crude oil (PBC), vacuum-stripped Prudhoe Bay crude oil (VSPBC), and reference oil (RO) calibration curves were used to obtain concentration values for each sample. The extraction step concentrates the oil in Freon (and CCl_4) by a factor of 10 over that concentration of oil in water (i.e., 1000 ml of sample extracted with 100 ml of solvent). Therefore, all values obtained from the calibration curves were divided by 10 to obtain the concentration of grease and oil in the sample.

After the infrared determination was performed, the IR sample aliquot was quantitatively transferred back to its respective volumetric flask and a gravimetric grease and oil determination performed using Method 502A. The results are tabulated in Table F-2. Analysis of the data reveals the following:

8-3-79 Treated Effluent Sample--

This sample contained 5.8 mgC/L with relatively low volatile hydrocarbon

TABLE F-1. PRUDHOE BAY CRUDE OIL RECOVERY, INFRARED ABSORBANCE METHOD

Log No.	Spiked Concentration (mg/L)	Solvent	Absorbance	Recovered Concentration (mg/L) PBC^1	VSPBC^2	RO^3	% Recovery PBC^1	VSPBC^2	RO^3
9-8-42	4.5	Freon	0.061	3.6	3.7	3.9	80	82	87
43	5.9	Freon	0.082	4.9	5.0	5.2	83	85	88
44	4.7	Freon	0.066	3.9	4.0	4.2	83	85	89
45	19.6	Freon	0.267	16.5	16.8	17.6	84	86	90
46	22.0	Freon	0.312	19.5	19.9	20.8	89	90	95
47	19.8	Freon	0.279	17.2	17.6	18.5	87	89	93
Average Recovery							84	86	90
9-8-70	4.9	CCl_4	0.083	3.6	3.5	3.7	73	71	76
71	4.7	CCl_4	0.082	3.5	3.5	3.6	74	74	76
72	5.3	CCl_4	0.088	3.8	3.8	3.9	72	72	74
73	19.9	CCl_4	0.321	17.6	17.5	18.2	88	88	91
74	19.8	CCl_4	0.323	17.7	17.6	18.4	89	89	93
75	20.2	CCl_4	0.333	18.4	18.2	19.1	91	90	95
Average Recovery							81	81	84

1. PBC - Prudhoe Bay crude oil standard
2. VSPBC - vacuum-stripped Prudhoe Bay crude oil standard
3. RO - reference oil standard

TABLE F-2. COMPARATIVE ANALYSIS OF TREATED BALLAST EFFLUENT

Chemical Composition, mgC/L		Triplicate Samples	Gravimetric Procedure: Freon Extraction	Gravimetric Procedure: CCl_4 Extraction	IR Procedure: Freon Extraction PBC[1]	IR Procedure: Freon Extraction VSPBC[2]	IR Procedure: Freon Extraction RO[3]	IR Procedure: CCl_4 Extraction PBC[1]	IR Procedure: CCl_4 Extraction VSPBC[2]	IR Procedure: CCl_4 Extraction RO[3]
		Samples of Treated Effluent, Collected August 3, 1979 — Oil and Grease Concentrations Found (mg/L)								
Chemical Composition, mgC/L:										
Nonvolatile Organics										
Suspended	0.6	A	1.7	2.0	1.8	2.0	2.0	1.8	1.8	1.9
Dissolved	4.4	B	2.0	2.1	2.1	2.3	2.3	2.1	2.1	2.2
Volatile	0.8	C	1.5	1.7	1.4	1.5	1.5	1.9	1.9	2.0
Total	5.8	Avg	1.7	1.9	1.8	1.9	1.9	1.9	1.9	2.0
Estimated mg/L	6.8	% Recovery	25	27	26	28	28	28	28	28
		Samples of Treated Effluent, Collected August 6, 1979								
Chemical Composition, mgC/L		A	3.6	3.9	4.3	4.4	4.6	4.6	4.6	4.8
		B	3.7	3.2	4.9	5.1	5.3	3.3	3.3	3.4
Nonvolatile Organics		C	3.3	3.0	4.0	5.2	4.3	3.5	3.5	3.6
		Avg	3.5	3.4	4.4	4.9	4.7	3.8	3.8	3.9
Suspended	6.8	% Recovery	20	20	26	28	27	22	22	23
Dissolved	3.4									
Volatile	4.3									
Total	14.5									
Estimated mg/L	17.0									

1. PBC - Prudhoe Bay crude oil standard
2. VSPBC - vacuum-stripped Prudhoe Bay crude oil standard
3. RO - reference oil standard

content (0.8 mgC/L). Approximately one-third of the total organic load was recovered by extraction into Freon 113 and carbon tetrachloride, followed by both IR and gravimetric quantification. Calibration curves based on three different types of standards produced essentially the same results. Extraction effectiveness of Freon 113 and carbon tetrachloride solvent appears to be very similar. Results obtained by the gravimetric method are very close to quantification based on the IR procedure. This consistency of results is probably due to the relatively low volatile hydrocarbon content of those samples.

8-6-79 Treated Effluent Sample--

This sample contained 14.5 mgC/L and volatile hydrocarbon fraction amounted to 4.3 mgC/L. Approximately one-fourth of the total organic load was recovered by the Freon extraction procedure, and one-fourth by the carbon tetrachloride procedure. Gravimetric recovery was in the order of 20%. Significantly, however, that IR procedure, based on Freon and carbon tetrachloride extraction, produced higher recoveries than the gravimetric procedure. The reason for the lower gravimetric recovery in this sample is probably due to loss of volatile hydrocarbon fraction during the evaporation step of the procedure.

Infrared Re-examination of Gravimetric Residue

The residue remaining after the gravimetric grease and oil determination was redissolved in its respective solvent, quantitatively transferred to a 100-ml volumetric flask, and made to volume. The solutions were then re-examined by IR to determine the subsequent grease and oil concentration. The results are presented in Table F-3. In all cases the determined values are considerably lower. Loss of volatile hydrocarbons, possible sample oxidation, and transferring losses are probably responsible for the lower values.

Comparison of Infrared Absorbance and Area Methods

Absorbance (peak height) measurement and area integration methods were used in the quantification of results. The results disclosed that the absorbance method results in recovery values that are equal to or higher than those obtained by the area measurement technique. Although the area technique is a practicable method, it appears to offer no advantage over the absorbance method. In addition, the area technique requires a sophisticated spectrometer capable of linear absorbance output as well as a means of integrating the area under the IR curve. For this study, it is felt that the absorbance values are more reliable than the area values.

REFERENCES

F-1. American Public Health Association. Standard Methods for Examination of Water and Wastewater. 14th Edition. APHA, Washington, DC. 1975.

TABLE F-3. INFRARED RE-EXAMINATION OF GRAVIMETRIC RESIDUE, INFRARED ABSORBANCE METHOD

Sample		Solvent	Absorbance	Grease and Oil Concentration (mg/L)*		
				PBC[1]	VSPBC[2]	RO[3]
8-3-79	A	Freon	0.023	1.4	1.6	1.6
	B	Freon	0.026	1.6	1.7	1.7
	C	Freon	0.020	1.2	1.3	1.3
8-6-79	A	Freon	0.043	2.6	2.8	2.8
	B	Freon	0.048	2.9	3.2	3.2
	C	Freon	0.040	2.4	2.6	2.6
8-3-79	A	CCl_4	0.025	1.0	1.0	1.0
	B	CCl_4	0.030	1.2	1.2	1.2
	C	CCl_4	0.025	1.0	1.0	1.0
8-6-79	A	CCl_4	0.056	2.4	2.4	2.5
	B	CCl_4	0.037	1.6	1.6	1.6
	C	CCl_4	0.039	1.7	1.7	1.7

* Corrected for sample volume.

1. Calculated using PBC calibration curve.
2. Calculated using VSPBC calibration curve.
3. Calculated using RO calibration curve.

APPENDIX G

AROMATICS IN OILY WASTEWATERS: DETERMINATION OF BENZENE, TOLUENE, AND XYLENES*

SCOPE

This method covers the determination of benzene, toluene, ortho-, meta-, para-xylenes and/or ethylbenzene in oily wastewaters. The dynamic range of the procedure is from 0.1 micrograms/liter (L) to 3 milligrams/L for individual hydrocarbons.

SUMMARY OF METHOD

Dissolved volatile hydrocarbons are purged from the oily wastewaters by nitrogen gas and adsorbed on activated charcoal by carbon disulfide. Reaction vessels equipped with Mininert valves are used for the desorption process. Front and back portions of the activated charcoal tubes are separated and transferred into different reaction vessels. One ml of carbon disulfide is introduced into the vessel by means of a syringe to prevent possible loss of volatiles due to heat of desorption. Known aliquots of carbon disulfide from the reaction vessels are injected into a gas-chromatograph and analyzed. A gas chromatographic procedure as described in this text or in ASTM ANSI/ASTM D2267-68 method (Ref. G-1) can be used for determining individual and total volatile aromatic hydrocarbons.

Calibration is performed by using synthetic blends of aromatic compounds. Typical retention times for principal volatile aromatic hydrocarbons found in oily wastewaters are shown in Table G-1 and a typical chromatogram is shown in Figure G-1.

NOTES

1. Reference should be made to ASTM Recommended Practice E260, General Gas Chromatographic procedures.
2. Light aromatic hydrocarbons are toxic. Special precautions should be taken when handling such materials to avoid inhaling the vapor. If some of the liquid is accidentally spilled on the skin, the affected part should be washed immediately with soap and water.

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* By Ihor Lysyj and Matthew Yoong, Rockwell International, Newbury Park, California.

TABLE G-1. TYPICAL RETENTION TIMES

Compound	Retention Time (minutes)
Benzene	5.0
Toluene	7.8
m-Xylene/Ethylbenzene	13.2
o-Xylene	15.8

APPARATUS

1. Sparging and Collection Apparatus. Glass vessels (1 to 2 liters in volume) equipped with glass, Teflon, or rubber stopper can be used for sample sparging. A gas dispersion tube of medium-porosity fritted glass and an adsorption train are inserted (gas-tight) into the stopper. The adsorption train consists of:

   a. A drying tube -- a 13-cm x 6-mm-ID glass tubing filled with 10/20 mesh Drierite with glass wool plugs at both ends

   b. An activated charcoal tube (MSA, 150-mg size) connected to the drying tube either with a short rubber tubing or a Swagelok glass-to-glass fitting

2. Chromatograph

   a. Concentration Range: The concentration range of benzene, toluene, and xylenes in primary and secondary effluents of ballast water is in the range of 0.3 to 5 mg/L. At least three point calibrations covering the indicated range should be performed. Samples containing higher concentrations of aromatic hydrocarbons are diluted or smaller sample volume size is used.

   b. Sample Inlet System: A sample inlet system that allows a constant volume of liquid sample to be injected.

   c. Column: Columns as described in ANSI/ASTM Method D2267-68 (Ref. G-1) can be used. In field studies, 3.66-m by 32-mm-OD stainless steel tubing packed with 5% OV-17 on 100/120-mesh Chromosorb W-HP was used. Other columns can be used provided, under conditions of the test, BTX can be resolved. Column conditions are tabulated in Table G-2.

3. Stripchart Recorder, 1 mV full scale.

4. Syringes - 1-microliter capacity. Additional syringes found to be useful: 5- and 10-microliter, and 1-milliliter capacity.

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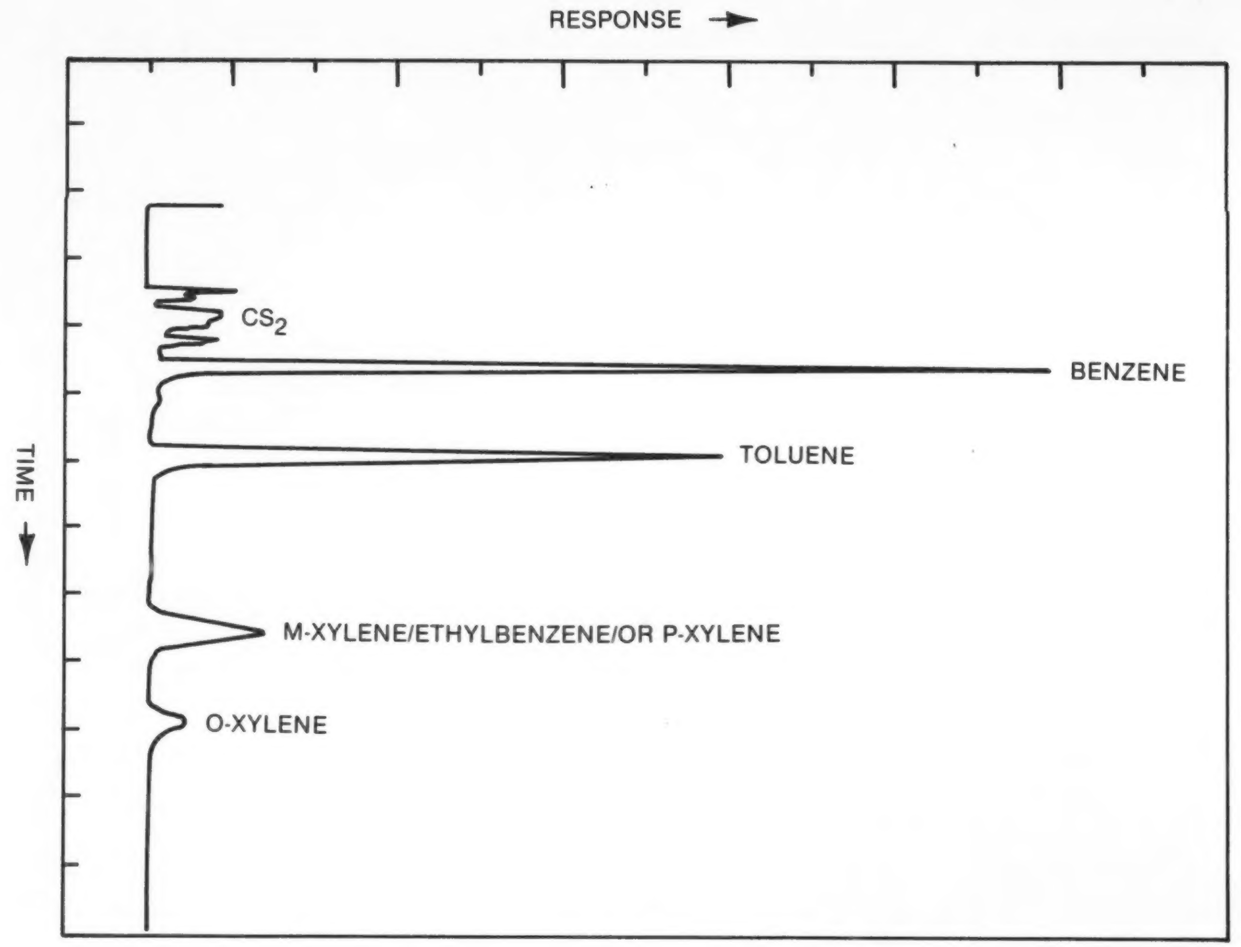

Figure G-1. Typical gas chromatogram of final effluent from ballast water treatment plant.

TABLE G-2. CONDITIONS OF ANALYSIS

Column:	
Liquid Phase	OV-17 (methyl-phenol silicone)
Weight Percent	5
Solid Support	Chromosorb W-HP
Mesh Size	100/120
Length	12 feet (3.66 meters)
OD	1/8 inch (0.32 cm)
Column Tubing	Stainless steel
Temperature:	
Sample Inlet System, °C	170
Detector, °C	170
Column, °C	80
Carrier Gas:	N_2
Flowrate (cc/min.)	20
H_2 Flow (cc/min.)	36
Air Flow (cc/min.)	180
Detector Type	HFID
Recorder Range, mv	1
Sample Size, microliter	1
Speed, cm/hr	30

5. Reaction Vessels and Mininert Vials - 2-ml capacity with sealed Teflon caps used in desorption operation.

6. Laboratory Equipment - volumetric flasks, volumetric pipettes, analytical balance, tubing, SS 1/8-inch OD.

7. Reagents and Materials

   a. Benzene, Reagent grade
   b. Toluene, Reagent grade
   c. m-Xylene, Reagent grade
   d. o-Xylene, Reagent grade
   e. Ethylbenzene, Reagent grade
   f. Carbon disulfide, Reagent grade

g. Activated charcoal tubes, MSA, 150-mg size
h. Drierite 10/20-mesh size

SAMPLE HANDLING

ASTM Method D-3325 for sample containers and preservation can be used. A 700- to 1000-ml sample of oily wastewater is normally used in the determination.

CALIBRATION

Calibrate the instruments as described in ASTM Method D-2267-68, or:

1. Prepare stock solution (by volume) of 1:1:1 mixture of benzene, toluene, m-xylene.

2. Prepare standard solutions by introducing:

    a. 75 microliters of stock to total volume of 50 ml of carbon disulfide

    b. 0.15 ml of stock to total volume of 50 ml of carbon disulfide

    c. 0.45 ml of stock to total volume of 50 ml of carbon disulfide

    mg/ml carbon disulfide equivalents of the above standard solutions are:

	Benzene	Toluene	m-Xylene
a.	0.44	0.43	0.43
b.	0.88	0.87	0.86
c.	2.64	2.60	2.59

3. Select instrument conditions from Standard Test Method ANSI/ASTM D-2267-68 or use the GC conditions shown in Table G-2. Inject a 1-microliter sample of each standard blend into the chromatograph. Each sample should be duplicated.

4. Measure the area of all aromatic peaks by any of the following means: triangulation, planimeter, paper cutout, ball-and-disc integrator or electronic integrator. Peak height measurement is acceptable when generated peaks are sharp and symmetrical.

5. Plot peak height or area of each individual aromatic peak versus concentration.

PROCEDURE

Introduce 700 to 1000 ml of oily water sample into sparging vessel. The vessel should be filled with water to no more than two-thirds of its volume. Purge the sample with 500 ml/min. flow of nitrogen for 30 minutes. At the end this period, remove adsorption (activated charcoal) tube and transfer the front and end portions of activated charcoal into two separate 2-ml reaction vessels equipped with Mininert Teflon caps.

Introduce 1 ml of carbon disulfide into each vial using a syringe. Allow the vials to stand at ambient temperature for 30 minutes with frequent shaking. At the end of 30 minutes inject a 1-microliter aliquot of each vial into the gas chromatograph. The instrument is operated under the same conditions as used during calibration.

CALCULATIONS

1. Measure the peak height or areas of aromatic hydrocarbons on chromatograph and read mg/ml equivalent directly from the calibration chart. Calculate the results as follows:

   $$\text{Concentration (mg/L)} = \frac{R \cdot S}{V}$$

   R = Reading from the calibration chart

   S = Sample size (microliters) injected into gas chromatograph

   V = Volume of oily water samples in ml

2. Total Aromatics: Add the amount of each aromatic compound found to obtain the concentration of total aromatics in the sample.

3. Report: Report concentration in mg/L to the nearest 0.1 mg/L.

APPENDIX H

PROCEDURES USED IN HARBOR STUDIES

NAVIGATION

The National Marine Fisheries Service (NOAA) diving support Rider-class vessel was used in this investigation. This vessel was equipped with a winch and steel cable for lowering and retrieving sampling devices from the required depths of the harbor. The sampling operations were carried out near the plant outfall in the Alyeska Marine Terminal in the security zone and at seven stations within Valdez Harbor.

The study required accurate positioning of the vessel at specified sampling stations. A triangulation method was used for locating sampling stations near the plant outfall. The method is based on the use of three shore reference points for locating each sampling station. The simultaneous measurement of two predetermined angles by two independently operated sextants pinpointed the location of the vessel (Figure H-1).

The following shore location points were used as aids in navigation:

	Coordinates*	
	N	E
1. Stack of terminal facility	2587664	431083
2. Point A at the east end of Berth No. 5**	2590426	429351
3. Point B at the east end of Berth No. 3**	2590813	432969
4. Point C at the west end of Berth No. 3**	2590272	432042
5. Point D at the east end of Berth No. 4**	2590088	430996
6. Point E second dolphin from east end of Berth No. 4	2590090	430791

The position of sampling stations in the area of the mixing zone were defined as follows:

Station 32, angle of 81° 37' between Point C and the terminal stack, and
angle of 40° 01' between Point D and the terminal stack

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* Alaska State Coordinate Grid, Zone 3.

** Navigation light at the end of berth was used as reference point.

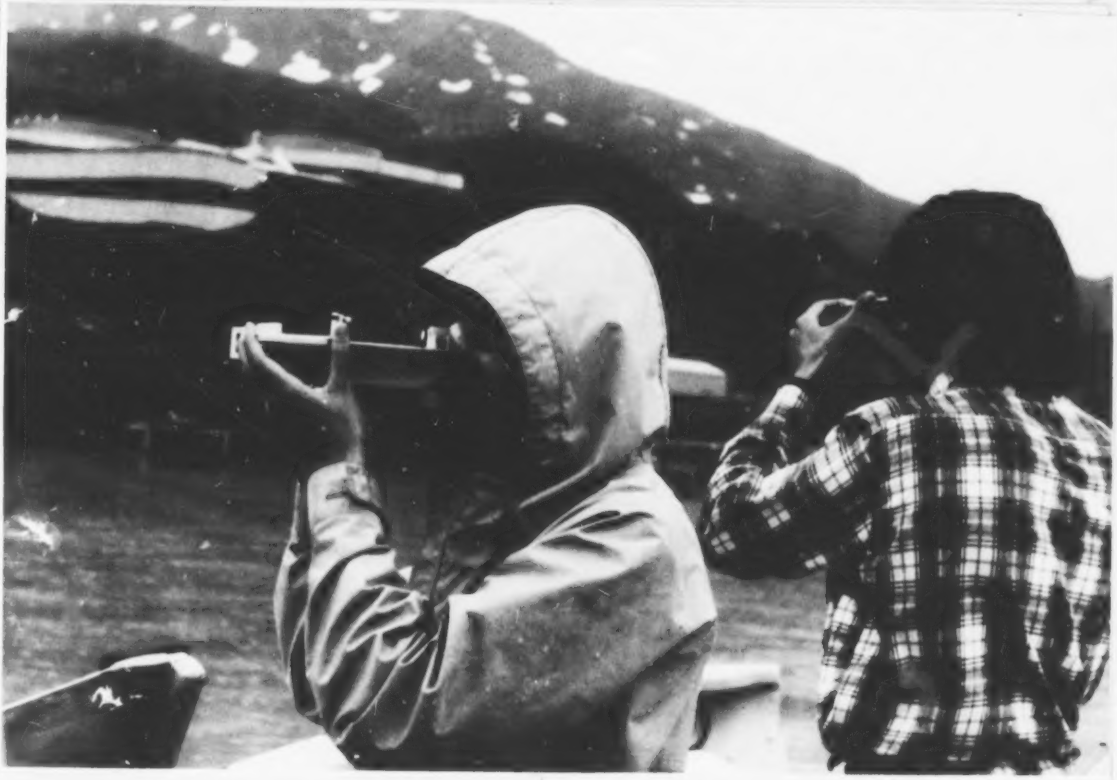

Figure H-1. Locating sampling stations.

Station 33, angle of 83° 50' between Points D and C, and
angle of 58° 36' between Points B and C

Station 34, angle of 40° 45' between Points C and D, and
angle of 95° 14' between Points B and C

Station 42, angle of 62° 9' between Points A and D, and
angle of 82° 17' between Points D and C

Station 46, angle of 68° 44' between Points B and C, and
angle of 42° 41' between Points C and D

Station 51, angle of 90° 0' between Points A and E, and
angle of 58° 30' between Points E and C

The position of harbor stations was as follows:

	Coordinates*	
Station	N	E
A	2592000	425400
B	2590500	400700
C	2596300	421100
D	2601800	419900
E	2590900	438400
F	2591700	446200
G	2595000	452300

SAMPLING

Depth samplers (Model XRB-135 manufactured by Hydro Products of San Diego, California) sere used for sample collection. The sampler is a cylinder with open ends that can be closed by snap covers triggered by release of a messenger. Two samplers located an appropriate distance from each other were used during field sampling operations. A winch equipped with a steel cable was used for lowering and retrieval of the sampling devices. The cable was measured and each 5-meter segment was appropriately marked. A view of the field sampling operation is shown in Figure H-2.

ANALYSIS

The analytical procedure used in this study was the same as described in Appendix F. The gas chromatograph, however, was operated at higher sensitivities (4×10^{-12} and 8×10^{-12}). Using this method and a Gow-Mac gas chromatograph, the detection limit for individual hydrocarbons was estimated at 0.1 microgram/liter, or 0.1 ppb. The quantification was performed using peak height measurement.

QUALITY CONTROL

Quality control implemented during this study included calibration, instrumental and procedural blanks determination, recovery, determination of lower limit of detection, and precision of the method. A sample of fjord water collected at Jackson Bay was considered to be a reference pristine water typical of Prince William Sound.

Calibration

Four-point calibration for benzene, toluene, m-xylenes and o-xylenes was carried out on September 18, 1979. Each analysis was performed in duplicate or triplicate and the calibration covered a 2- to 41-ppb concentration range for each of the specified aromatic hydrocarbons. All calculations reported here are based on an 850-ml water sample, the organic matter of which was

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* Alaska State Coordinate Grid, Zone 3.

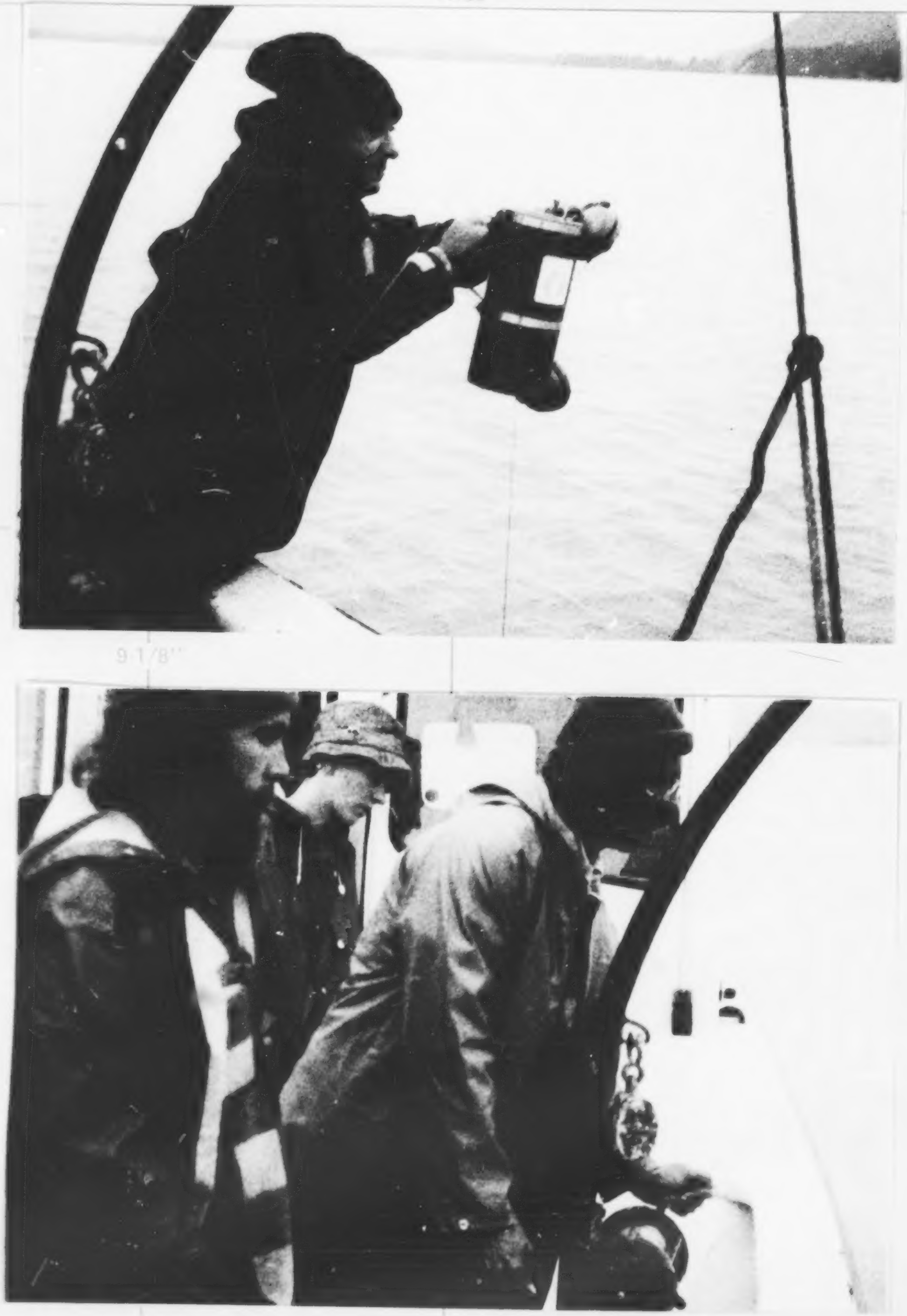

Figure H-2. Sampling operations.

concentrated into 1 ml of carbon disulfide, providing an 850-fold increase in concentration.

The calibration data is tabulated in Table H-1 and displayed graphically in Figure H-3 (the low concentration range) and Figure H-4 (expanded scale). The reported data reveals that response of the gas chromatograph in the 0 to 40 ppb concentration region is linear, and the procedure is reproducible to ±5%. For this reason, one- or two-point calibration appears to be sufficient for accurate determination.

Lower Limit of Detection

The lower limit of detection is normally defined as a signal twice the baseline noise or otherwise measurable quantity. The instrumental noise of

TABLE H-1. CALIBRATION DATA

Compound	Standard Solution mg/L	Equivalent to µg/L (ppb) in 850-ml Sample	Response in mm Normalized at Sensitivity 4×10^{-12}			
			9-18-79	Avg	9-19-79	Avg
Benzene*	1.8	2.1	98, 100, 101	(100)		
	3.5	4.1	208, 212, 216	(212)	244, 236	(240)
	14.0	16.4	752, 720	(736)	726, 726	(726)
	35.0	41.0	1952, 1952	(1952)		
Toluene	1.8	2.1	61, 62, 60	(61)		
	3.5	4.1	126, 126, 128	(127)	138, 136	(137)
	14.0	16.4	464, 448	(456)	468, 468	(468)
	35.0	41.0	1264, 1248	(1256)		
m-xylene	1.7	2.0	35, 35, 34	(35)		
	3.4	4.0	70, 69, 71	(70)	74, 74	(74)
	13.8	16.0	258, 254	(256)	262, 260	(261)
	34.4	40.0	688,672	(680)		
o-xylene	1.8	2.1	28, 27, 26	(27)		
	3.5	4.1	58, 57, 57	(57)	60, 60	(60)
	14.0	16.4	236, 232	(234)	216, 216	(216)
	35.0	41.0	568, 560	(564)		

* Compensated for solvent blank.

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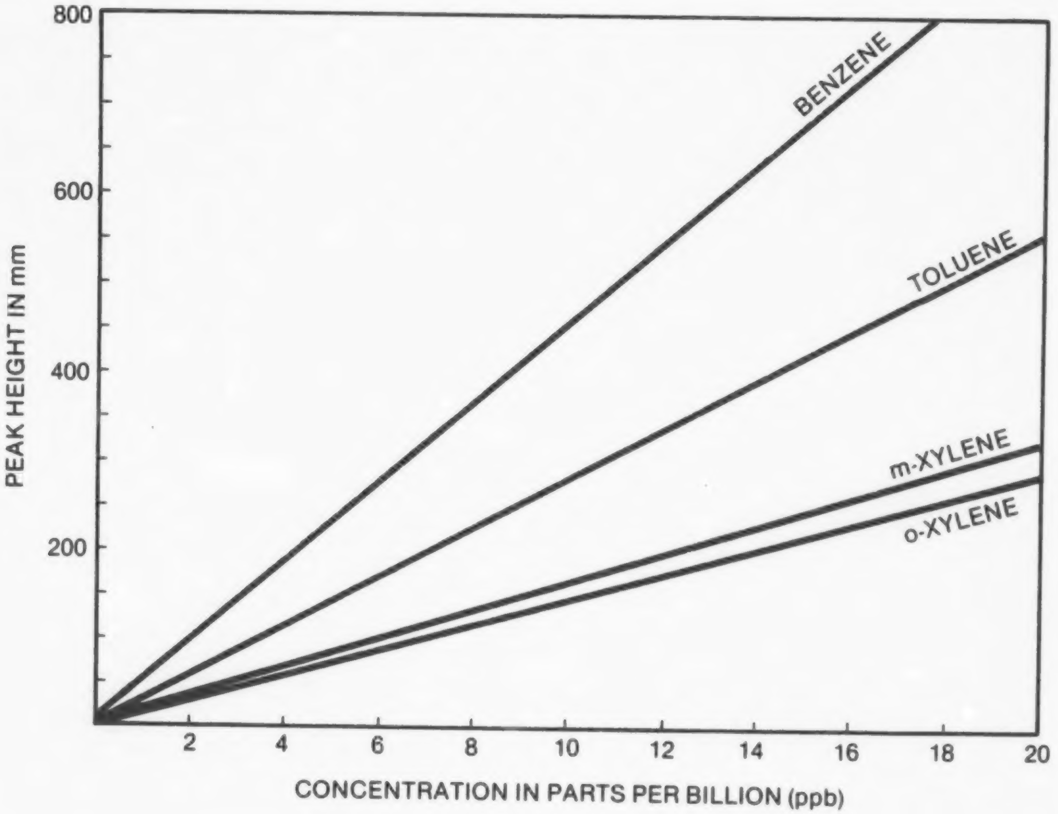

Figure H-3. Calibration curve for aromatic hydrocarbons: low concentration range.

the Gow-Mac gas chromatograph, when operated at sensitivities of 8×10^{-12} and 4×10^{-12}, is insignificant (see chromatograms in Figure H-5), and for this reason the measurable peak height of 2 mm was defined as the least detectable quantity. The mean values (duplicate or triplicate) for peak height which are proportional to concentrations of 1 ppb of benzene, toluene, m-xylene, and o-xylene, are shown in Table H-2. Examination of this table indicates that the range of responses for 1-ppb concentration at a sensitivity of 4×10^{-12} is from 14 mm (o-xylene) to 49 mm (benzene). Assuming the detectable limit has a peak height of 2 mm, this would correspond to a detection limit range of 0.04 to 0.14 ppb for individual aromatic hydrocarbons.

Reproducibility (Precision)

Reproducibility data for six analyses (duplicate or triplicate determinations per analysis) are reported in Table H-2. The reported data indicates that the precision of the method in the 0.5- to 40-ppb concentration range is between ±4% and ±8% for individual aromatic hydrocarbons.

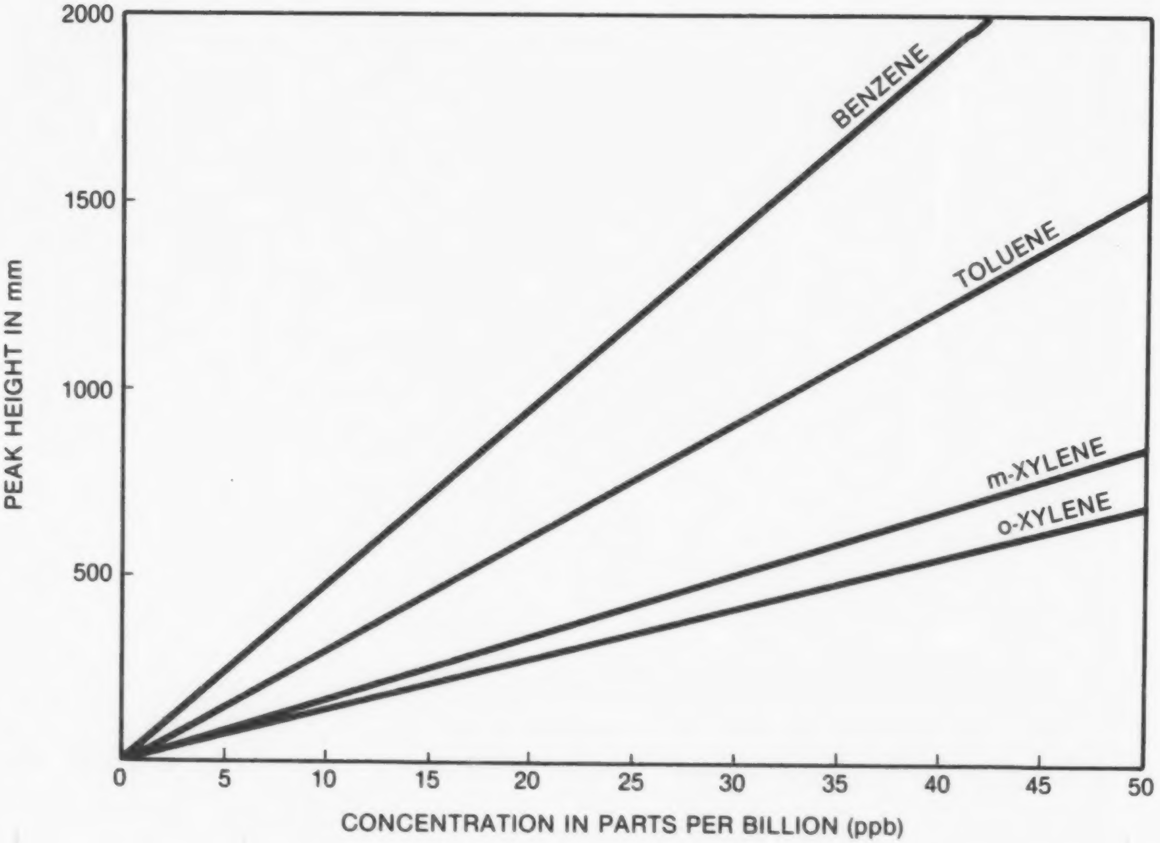

Figure H-4. Calibration curve for aromatic hydrocarbons: expanded scale.

Contamination Control

The trace analysis in the low-ppb concentration range required close contamination controls. Instrumental and procedural blank determinations were performed to assure the absence of false-positive contributions.

The instrumental blanks were performed daily before initiation of calibration and analysis. One ml of carbon disulfide was injected in the gas chromatograph and analyzed in the same manner as standard calibration solutions and unknown samples. A typical gas chromatogram of an instrumental blank is shown in Figure H-5. A small peak was usually observed for benzene, and this value was compensated for in all subsequent calculations. No instrumental blank response was observed for toluene or xylenes.

The procedural blank determination involved preparing synthetic sea water, which was introduced into the sampling container (used in field work) to simulate the sampling operation, and then carrying out the procedural operation in exactly the same manner as in the analysis of "real-life" samples. This

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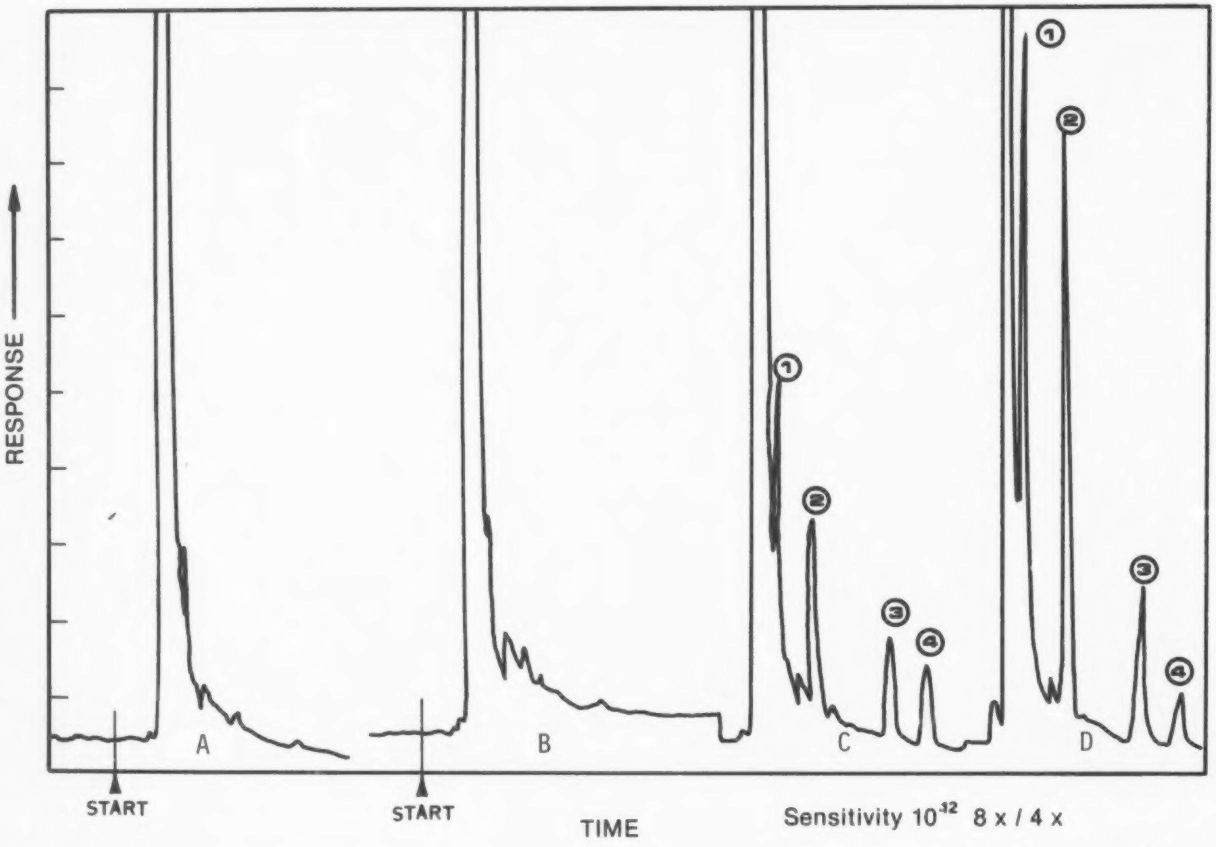

Figure H-5. Gas chromatograms of volatile hydrocarbons at ppb concentration levels.

(A = instrumental blank, B = procedural blank, C = standard solution 2 ppb each: (1) benzene, (2) toluene, (3) m-xylene, (4) o-xylene, D = harbor water, Station 34, depth 76 meters)

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TABLE H-2. REPRODUCIBILITY OF RESULTS

(Response to 1 ppb in mm at 4 x 10^{-12} sensitivity)

Compound	Peak Height in mm	Average	Standard Deviation
Benzene	48, 52, 45, 48, 59, 44	49	±6
Toluene	29, 31, 29, 31, 33, 28	30	±2
m-xylene	18, 18, 16, 17, 19, 16	17	±1
o-xylene	13, 14, 14, 14, 15, 13	14	±1

analysis produced the following blank values: benzene peak height, 2 mm; toluene peak height, 7 mm; m-xylene peak height, 3 mm. The gas chromatograms for procedural blanks are shown in Figure H-5. In terms of concentration, they correspond to: benzene, 0.04 ppb; toluene, 0.25 ppb; m-xylene, 0.19 ppb -- or approximately 0.5 ppb of total aromatic hydrocarbons.

During the period of exploratory field and laboratory work, this value was designated as a practical lower limit of detection and a practical measure of the method's precision. Correspondingly, all values reported here for total aromatic hydrocarbon content should be considered valid within ±0.5 ppb.

Recovery

Recovery studies on benzene, toluene, m- and o-xylenes at low concentrations (2 ppb) were carried out in January 1980. The standard test solution was prepared in the following manner: n-hexane, benzene, toluene, m-xylene and o-xylene mixture was prepared in a 1:1:1:1 volume by volume ratio. One microliter of the mixture was injected into a 500-ml volumetric flask. The flask was placed into an ice bath and stirred for 20 minutes with a magnetic stirrer. A stock solution was kept refrigerated. A measured amount of the stock solution was added to an 850-ml sample of synthetic sea water immediately before sparging. Results are reported in Table H-3.

Based on this experimental data, it appears that recoveries of 70% to 80% can be realized for BTX at the low end of the operational procedure described here, with reproducibility of approximately ±5%.

REFERENCES

H-1. ANSI/ASTM Method D2267-68. American Society for Testing Materials. Philadelphia, Pennsylvania.

TABLE H-3. RECOVERY DATA FOR BENZENE, TOLUENE, M- AND O-XYLENES (BTX), JANUARY 1980

Compound	Sample Size (ml)	Concentration (ppb)	Amount Present (μg)	Amount Found (μg)
Benzene	850	2.07	1.76	1.54
	850	2.07	1.76	1.85
	850	2.07	1.76	1.19
	850	2.07	1.76	1.19
	850	2.07	1.76	1.46
	850	2.07	1.76	1.48
	850	2.07	1.76	1.38
Mean and Standard Deviation				1.44 ±0.23 μg
Recovery and $\delta/\sqrt{n}$				82 ±5%
Toluene	850	2.03	1.73	1.63
	850	2.03	1.73	1.72
	850	2.03	1.73	1.24
	850	2.03	1.73	1.38
	850	2.03	1.73	1.49
	850	2.03	1.73	1.43
	850	2.03	1.73	1.45
Mean and Standard Deviation				1.48 ±0.16 μg
Recovery and $\delta/\sqrt{n}$				85.4 ±3.5%
m-Xylene	850	2.03	1.73	1.03
	850	2.03	1.73	1.36
	850	2.03	1.73	0.61
	850	2.03	1.73	1.09
	850	2.03	1.73	1.26
	850	2.03	1.73	0.91
	850	2.03	1.73	1.17
Mean and Standard Deviation				1.06 ±0.25 μg
Recovery and $\delta/\sqrt{n}$				61.4 ±5.4%

(continued)

TABLE H-3 (Continued)

Compound	Sample Size (ml)	Concentration (ppb)	Amount Present (μg)	Amount Found (μg)
o-Xylene	850	2.07	1.76	0.66
	850	2.07	1.76	0.93
	850	2.07	1.76	0.22
	850	2.07	1.76	0.76
	850	2.07	1.76	0.89
	850	2.07	1.76	0.50
	850	2.07	1.76	0.44
Mean and Standard Deviation				0.69 ±0.25 μg
Recovery and $\delta/\sqrt{n}$				39 ±5.4%

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